



Food Engineering

Research Developments



Terrance P. Klening
Editor

NOVA

FOOD ENGINEERING RESEARCH DEVELOPMENTS

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PREFACE

Food engineering refers to the engineering aspects of food production and processing. Food engineering includes, but is not limited to, the application of agricultural engineering and chemical engineering principles to food materials. Genetic engineering of plants and animals is not normally the work of a food engineer. Food engineering is a very wide field of activities. Among its domain of knowledge and action are: Design of machinery and processes to produce foods Design and implementation of food safety and preservation measures in the production of foods Biotechnological processes of food production Choice and design of food packaging materials Quality control of food production. This new book deals with food engineering research from around the globe.

Chapter 1 - Food processing is an indiscrete part of the chain from cultivation/catch to consumer. During the last decades the food value chain has grown longer and has become more market oriented, i.e. consumer driven instead of producer driven. New information on the effects of food on the health of the consumers and on the environment will continue to influence the choice of consumers regarding food products.

Emphasis on knowledge has and will continue to increase accordingly when producing and marketing food products. The consumer demands knowledge on the origin of the product, on the environmental effects of the production as well as effects on the communities where the production takes place, i.e. the emphasis is on solicitude. At the same time the product should be convenient to cook, safe and fresh. This calls for consistent research and development where the focus in the next years will be on the following areas:

- Fresh products, cooling instead of freezing - superchilling
- Process optimisation, based on precise measurements (such as NMR) and historical data on raw material.
- New processing methods, aiming at minimum processing while ensuring safety at the same time
- Improved use of byproducts
- Engineered products – functional foods
- Low energy use in production
- Supply chain management, including optimisation of transportation
- Genetic improvements of crops and farmed animals.
- Traceability

- Verification of sustainable and/or organic production, fair and ethical trade as well as other solicitude matters.
- Marketing differentiation
- Increased dissemination of research results and other information to consumers
- OR
- Statistics

Besides from these areas, merging of research institutes and universities will also characterize the food engineering research environment the next decade, as well as increased cooperation between research parties and industrial companies.

The authors will discuss this development, the focus of leading food engineering researchers in Iceland with regard to this development and what strategic aim Matis ohf and the University of Iceland will take to ensure their competitiveness in this fast developing area.

Chapter 2 - Water is the most important compound of food. It affects chemical reactions, microbial growth and organoleptic quality. Historically, the effects of water on food degradation have been related to its availability but the lack of exact definition of this term has caused contradictory results. Nevertheless, it is well known that through the control of “free” and “bound” water content it is possible to restrict degradation reactions and to improve food quality.

Nowadays different parameters to measure the state of water in food are available but, from industrial point of view, the most important is the water activity (a_w). This term is used to indicate the ratio of the vapour pressure in equilibrium with a food and the vapour pressure of water at the same temperature and pressure. With the recognition of the importance of this parameter, new knowledge and understanding of water-food interaction have led to new methods to obtain shelf-stable food by reduction of water activity. Moreover, the importance of water activity led food scientists to study mathematical models to predict a_w values in complex food.

In this chapter the authors present results about osmodehydration and direct addition of humectants as treatments to reduce water activity in food. The authors studied, in particular: i) the interactions of different humectants, the influence of process variables and the development of mathematical models to predict a_w values from a statistical and engineering point of view; ii) the optimization of processes with the aim to obtain safe vegetable food with good organoleptic quality. Also, the authors reviewed the new water-food interaction theories based on dynamic rather than thermodynamic. In particular, the authors analyze the glassy transition temperature and translational diffusion coefficients measured by DSC and NMR techniques and present some preliminary results obtained on apple osmodehydrated samples.

Chapter 3 - This chapter is aimed to underline the increasing importance that natural antioxidants have been gaining in the last years. Antioxidants are naturally present in many foods, so that they can be seen as potential recovery sources: oilseeds, nuts, cereals, legumes, vegetables, fruits, herbs, spices and teas. Besides these, antioxidants are often present in food processing by-products and wastes, so that the employment of low-cost industrial wastes could greatly reduce the production costs and increase the margin profit of the products. The introductory section summarises the classes of antioxidant compounds (mainly focusing on phenolic compounds), their potential food and no-food applications, and the main problems

you have to account for when recovering antioxidants from residual sources, such as selection of a suitable agriculture by-product, choice and optimisation of the extraction procedure, analytical characterisation and evaluation of antioxidant activity of the obtained extracts, evaluation of potential applications of the isolated substances.

The second part of the chapter presents an experimental work dealing with recovery of phenolic compounds from wine-making wastes through a simple solvent extraction process. Trials were carried out in order to evaluate the feasibility of using different by-products (grape stalks, grape marcs before and after distillation), the influence of grape variety, of different sample pre-treatments, type of solvent, extraction temperature and time (extraction kinetics) on extracts yield and quality in terms of phenolics content and antioxidant power. Food applications of the obtained compounds to inhibit oil oxidation and to extend shelf-life of fresh fruits were also investigated.

Chapter 4 - Mathematical modeling represents a very important and effective tool for a proper design and control of industrial processes. A model reliably predicting a particular transformation process can, in fact, be used to investigate how the outputs may change with time under the influence of changes of the external disturbances and manipulated variables. In this way, it is possible to optimize the process, thus improving the quality and the safety of the final product. A mathematical model is, generally, based on a relationship, expressed in form of an equation (or a system of equations), whose solution yields the dynamic or static behavior of the process under examination. Both finite element method (FEM) and finite difference (FD) modeling have been utilized in food engineering research. A detailed analysis of the literature in the last 15 years shows that FEM applied to heat transfer dominates the publications, followed by diffusion calculations and drying process simulations. It is to be remarked, however, that a widespread use of mathematical modeling in food engineering is far from being well assessed.

The main aim of the present chapter is to analyze the transport phenomena involved in food drying process, performed in a convective drier. The formulation of two different theoretical models will be presented, focusing the attention on the differences that may be obtained if a simplified or a more complete analysis of the same transport problem is adopted. Both the models describe the simultaneous transfer of heat and moisture occurring during drying process. Actually, the first approach is much simpler, even though it could be considered a very important advance with respect to the theoretical analyses that are currently available in the literature. On developing the “simple” model, only food domain has been taken into consideration; moreover, heat and mass transfers occurring at the food surface exposed to the drying air have been estimated on the basis of a set of semi-empirical correlations available in the literature. The second model, instead, takes into account also the behavior of the drying air flowing, in turbulent conditions, about the food sample. This approach is, therefore, more general since it describes the simultaneous transfer of momentum (for air only), of heat and mass (for both air and food) occurring in a convective drier and does not need the specification of any heat and mass transfer coefficient at the food-air interface that, indeed, is one of the results of the proposed model.

Both the models receive - as inputs - only the initial conditions, the geometrical characteristics of both food and drying chamber and the relationships expressing physical and transport properties of food and air in terms of the local values of temperature and moisture content. The resulting system of non-linear, unsteady-state partial differential equations has been solved by means of the Finite Elements Method. The comparison between two possible

different approaches may suggest if a significant increase of computation effort is actually required or, instead, if the utilization of a much simpler and faster method is capable of giving a proper description of the process under consideration. The main objective of the present work is to show how an accurate transport model can be used to determine the influence of operating conditions on drying process. In this way, it might be possible to minimize expensive pilot test-runs and have good indications on the characteristics and the quality of dried products.

Chapter 5 - Drying food is an extremely sensitive operation that requires the proper monitoring and control of the heating medium temperature as well as the length of time that the product is exposed to this temperature. Since the different food products have different heat sensitivity the heat load tolerance during drying cannot be generalized if loss of quality is to be avoided. On the other hand the drying process is a very high energy consuming operation and energy usage must be minimized without necessarily compromising on product quality. Optimization of a drying process requires that the authors consider the heat and mass transfer dynamics, product quality indices and production costs. Different control strategies and objective functions must be tried because it would not make business sense to produce a very high valued product at astronomical costs to the producer and nor would a low quality product sell simply because it is produced at minimum cost or energy consumption. This Chapter reviews first the research trends on modeling of the drying process based a heat and mass transfer, cost of drying and product quality. The strategic logistics that have been used over the years in attempts to optimize the drying operation have also been reviewed. Last but not least, the performance of these dryer control strategies in the practical optimization of the drying process have been discussed since it is how well a control strategies works that can make the entire optimization process either a success or a failure.

Chapter 6 - Canned foods are a significant component of the diet of most people in both developed and developing countries, offering a wider choice of nutritious, good quality foods in a convenient form all-year-round. During canning, both desirable and undesirable changes occur in nutritional and sensory properties of foods, resulting from heat treatment employed for the destruction of microorganisms to achieve the desired commercial sterility. The extent of thermal processing, in terms of both temperature and duration of the treatment, is dependent upon the chemical and physical composition of the product, the canning medium and the conditions of storage, determining the product quality in terms of its sensory properties and nutrient content. This chapter reviews the major principles and operations used during food canning, identifies the nutritional and sensory changes occurring during the process and their effect on the quality of canned foods. In addition, it explains the use of response surface methodology (RSM) as modelling and optimization techniques used in the canning industry in recent times to manipulate canning processes to maintain the nutritional and sensory qualities of canned foods, using two recent studies where RSM was used to study the effect of pre-canning processes including blanching time, soaking time and sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ salt concentration on moisture, minerals, leached solids, phytates, tannins and hardness (texture) of cowpeas (*Vigna unguiculata*) and bambara groundnut (*Voandzei subterranea*). Regression models were developed to predict the pre-canning parameters that yield the best quality products, with minimal effects on the nutritional and textural properties of the products. The optimal conditions found to achieve the optimum quality of the canned cowpeas were blanching time of 5 min, soaking time of 12 h and $[(\text{NaPO}_3)_6]$ salt concentration of 0.5%, and for the bambara groundnut; blanching time

of 8 min, soaking time of 12 h and $[(\text{NaPO}_3)_6]$ salt concentration of 0.5%. The combination of blanching, soaking and $[(\text{NaPO}_3)_6]$ salt were modeled using RSM to retain the nutritional (mineral) content of products while reducing the anti-nutritional factors and the hardness of the canned products with acceptable quality characteristics, indicating that as recent advances in canning technology, modelling techniques could be used to control canning operations while retaining desirable product quality characteristics.

Chapter 7 - Starch and proteins processed as individual components offer a wide range of functional properties. Unique blends can be prepared by the extrusion process with a synergistic effect inducing cross-linking sites that contribute to the protein three-dimensional network stability after extrusion, affecting nutritional and functional properties of the new biopolymer to be used in diverse food systems. The aim of this work was to study the effects of extrusion variables such as barrel temperature, feed moisture, alkaline and acidic pH, different proportions of corn starch (CS) and whey protein concentrate (WPC) on protein surface hydrophobicity (S_o), degree of denaturation, rheology, and physicochemical properties of the functional blends. The extrusion variables were barrel temperature (BT 70-180°C), feed moisture (FM 18-30%), pH (3-8) and the ratio of WPC to CS. The physicochemical characterization showed that FM and pH had significant effect on expansion index (EI); EI increased with lower values of FM and higher pH. An interaction of BT and FM had an effect on water absorption index (WAI); at lower FM, the BT effect was nonexistent, whereas at higher BT and higher FM, the WAI increased. PH had a significant effect on WSI, showing high WSI when low pH levels were used. Color analysis showed that higher protein content and pH generated color difference values (ΔE); low FM and low pH resulted in gel syneresis. The highest *in vitro* digestibility was obtained when a higher WPC proportion and pH were used. Surface hydrophobicity (S_o) is a good indicator of the hydrophobic side groups available for interactions in food systems. S_o was affected by the extrusion parameters; this information was used to monitor the interaction between proteins and carbohydrates present in the blends. Reversed-phase chromatography was used to evaluate denaturation of protein after extrusion. Although in extrusion denatured protein, S_o values for the blends were lower than those of the individual components. Rheology reinforced these results. The extruded blends of starch-WPC have potential to be utilized in milk-based new food products such as Oaxaca-type cheese analogues and drinking yoghurt-like.

Chapter 8 - In order to guarantee and optimize the quality of a good cup of coffee, roasting is a key step in the process. In this roasting step the green beans are heated at high temperatures (over 190 °C), initiating a series of complex chemical reactions, which lead to the formation of essential substances to give among other, the sensory quality of the cup of coffee. Consequently, roasting is essential to control a large number of factors. Today's, robust sensors and algorithms are used to measure and on-line analyze essential factors such as color, surface, temperature, weight,... In this work, a control strategy is applied to on-line estimate the quality of roasted coffee. Coffee beans were roasted using hot air as heating medium. Bean temperature, weight, color and surface were measured on-line during roasting. These experiences allow better understanding of the phenomena that appear during roasting. A dynamical model was used to describe the heat and mass transfer of the beans while the gray values and expansion kinetics of the beans were estimated by an artificial neural network. The neural network considers the simulated temperature of bean and roasting time during the process. This strategy allowed us to estimate the quality of roasted coffee, when

the roasting degree wished is similar to the gray value obtained by the model. These results were in good agreement since the roasted coffee was evaluated experimentally. Therefore, it is possible to apply this strategy in the industry to guarantee the quality of coffee roasting.

Chapter 9 - The selection of appropriate fibres is determined by the required values of the stiffness and tensile strength of a biodegradable material. Further criteria for the selection of suitable reinforcing fibres are, for example, elongation at failure, thermal stability, and adhesion of fibres at the matrix (starch), dynamic and long-term behaviour, price and processing costs. The fibres can impart synergistic properties to the thermoplastic starch composition. The aim of this research was to study the effects of extrusion variables: feed moisture, barrel temperature and content of sugar cane fibre, starch and plasticizer on the mechanical properties of traction of films that can be used for the manufacturing of disposable bags. Sugar cane fibre (250 μm) and native starch (25% amylose) were used as starting materials. An experimental laboratory single screw extruder with an L/D ratio of 20:1, designed and manufactured by Cinvestav-IPN, México.

A screw compression ratio of 1:1, and a rectangular die-nozzle of dimensions 40 mm X 0.75 mm were used. Feeding and die zones temperatures were kept constant at 60 and 75°C respectively; whereas the temperature of the transition zone (zone 2) was set according to the experimental design (110-140°C). The screw speed was kept constant at 40 rpm. The extruded films were stored for 40 h under controlled temperature and humidity (23 $\pm$ 2°C and 50 $\pm$ 5%) for further analysis. The evaluated properties of traction were: Maximum resistance to the traction (σ_{max}), Elongation at fracture (ϵ_f): and Modulus of elasticity (E) according to standard ASTM-D882-00. It was found that high plasticizer content (>30%) decreased the σ_{max} . On the other hand, intermediate fibre content (5-15%) increased the σ_{max} ; high barrel temperatures (130°C) and intermediate fibre contents favored the ϵ_f and therefore resulted in thinner films. Also, high fibre contents (>15%) and low feed moisture (18.25%) decreased E which resulted in a less flexible film. The best conditions for thermoplastic extrusion were found to be: Barrel temperature (110-130°C), feed moisture (20.5-22.75%), fibre content (5-15%) and plasticizer (22-30%) as shown in assays 3, 5, 7, 8, 11, 12, 15, 16, 25, 30. In summary, fibres can impart more strength to the starch-bound matrix without adding significantly bulk or mass to the matrix. Sugar cane fibre in blends with native starch improved the strength and other mechanical properties of the films, and it has strong potential for the production of disposable bags.

Chapter 10 - Diverse formulations of thermoplastic biopolymers have been developed in an attempt to at least partially replace non-degradable petroleum-based products with biodegradable components which can be used for the manufacture of extruded and/or moulded articles such as films, utensils, containers, electric appliances and automobile interior materials. Several of these materials have been formulated of blends of starch and other components. In general, such thermoplastic biopolymers that have been developed primarily for the packaging industry do not have the mechanical characteristics of conventional polymers. In particular, the high rigidity and fracturability are disadvantageous for this projected usage. In addition, these materials tend to interact among them, this causes that the materials loss their dimensional stability, and tear or collapse. In an attempt to improve the structural stability of articles made from starch-based compositions, the authors experimental research have shown the viability of the use of natural fibres as reinforced materials in blends with native corn starch. The use of starch blended with agricultural fibres

result attractive because the final products have the advantages of low cost, low density, acceptable specific strength properties, and biodegradability. Also, in many Latin American countries there are available high volumes of agricultural residues that can be used as raw materials to fabricate biodegradable materials. In this work, the effect of fibre and glycerol contents in blends with native corn starch on structural and mechanical properties of extruded injected-moulded plates was evaluated. Mechanical properties (elasticity modulus), structural properties (X-ray diffraction, viscosity profiles, infrared spectroscopy, scanning electronic microscopy) and biodegradable properties were evaluated in extruded injected-moulded plates. These plates showed better mechanical properties when increasing the fibre content, improving their resistance. Also, increasing the glycerol content improved the elongation and processability in plates. Structural properties (X-ray diffraction), viscosity profiles, infrared spectroscopy and scanning electronic microscopy (SEM) showed some changes in the physical structure of the materials as well as the possible interaction of fibres with the polymeric starch matrix. Studies of biodegradation showed that the fabricated plates were completely biodegradable. The best mechanical properties of the plates were those that had a formulation of 10% of fibre and 10% of glycerol with starch. It becomes clear that some of these natural fibres can potentially be used as reinforced material in blends with native starch with similar characteristics to those fabricated with conventional polymers.

Chapter 11 - Commercial food flavors in liquid form are difficult to handle or incorporate into foods. Flavors are volatile and thus would readily evaporate from a food matrix during storage. Encapsulation provides a better retention of flavors and protection against light-induced reactions and oxidation. Various forms of modified starches are used for flavor encapsulation which includes emulsifying starches and starch hydrolysis products. The aim of this work was to prepare phosphorylated waxy maize starch by melting extrusion with sodium tripolyphosphate using a single-screw extruder, and its evaluation as shell material for encapsulation of orange peel oil using spray drying. Starches were hydrolyzed with hydrochloric acid before they were esterified (3.4% HCl, 6 h, 50°C). The viscosity of the modified starch was reduced as the hydrolysis products had smaller molecular weights than the native starch, while the water solubility index increased, making the modified starches appropriate for the encapsulation process using spray drying. Emulsions were prepared with 30% (w/w) of shell material and 20% of orange oil (w/w) by weight, based on the total weight of solids. The phosphorylated starch had a total oil retention of 55.7%. The addition of 2% (w/w) of whey protein concentrate (WPC) improved the emulsification process and oil retention to 66.8%. Encapsulated orange peel oil showed a good stability through 28 days of storage at room temperature and 50°C (50% HR) with an oil retention of 86% and 68% with respect of the starting oil in the capsules. The use of blends of starch-WPC improved the emulsification process and oil retention during spray-drying. Phosphorylated starches are a good alternative of shell material of low cost for flavor encapsulation.

Chapter 12 - This paper aimed to make a longer-term forecast analysis on global food nutrition supply and demand. The forecasts of supplies of food calories and proteins for the world and various regions over the period 2010-2030 were given, and food nutrition supply and demand balance in the forecast period was discussed.

If the past pattern continues, the global total food calorie supply would grow at the annual rate of 13.43 ± 0.71 kcal/cap/day and reach 3210.4 ± 67.3 kcal/cap/day in 2030. Total food calorie supplies for all of the regions would grow during the forecast period and, in most regions they are forecast to be greater than 3000 kcal/cap/day from 2015-2020. Total food

protein supply for all regions but not Oceania, is forecast to grow during the forecast period. The proportion of animal sourced protein in total food protein supply is in 2030 forecast to increase and reach 35.5%, 61.6%, 56.8%, and 21.7% for Asia, Europe, South America, and Africa.

Food calorie supply in the world is expected to exceed the adequate energy intake after around 2015. Strong focus should be worldwide put on the over-intake of food calorie in the near future. Global food protein supply is not expected to be greater than the adequate range during the period 2010-2030. Food protein supply in Africa and Caribbean would be just a little greater than the basic demand in the forecast period. Food protein intake in these regions should be improved in the coming years.

Chapter 1

FOOD ENGINEERING TRENDS – ICELANDIC VIEW

***Sveinn Margeirsson^{1,2}, Gudmundur R. Jonsson²,
Sigurjon Arason^{1,3}, Gudjon Thorkelsson^{1,3}, Sjöfn Sigurgísladóttir¹,
Birgir Hrafnkelsson⁴ and Páll Jensson²***

¹Matis ohf

²University of Iceland, Department of Mechanical and Industrial Engineering

³University of Iceland, Department of Food science

⁴University of Iceland

Abstract

Food processing is an indiscrete part of the chain from cultivation/catch to consumer. During the last decades the food value chain has grown longer and has become more market oriented, i.e. consumer driven instead of producer driven. New information on the effects of food on the health of the consumers and on the environment will continue to influence the choice of consumers regarding food products.

Emphasis on knowledge has and will continue to increase accordingly when producing and marketing food products. The consumer demands knowledge on the origin of the product, on the environmental effects of the production as well as effects on the communities where the production takes place, i.e. the emphasis is on solicitude. At the same time the product should be convenient to cook, safe and fresh. This calls for consistent research and development where the focus in the next years will be on the following areas:

- Fresh products, cooling instead of freezing - superchilling
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- Verification of sustainable and/or organic production, fair and ethical trade as well as other solicitude matters.
- Marketing differentiation
- Increased dissemination of research results and other information to consumers
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- Statistics

Besides from these areas, merging of research institutes and universities will also characterize the food engineering research environment the next decade, as well as increased cooperation between research parties and industrial companies.

Our chapter will discuss this development, the focus of leading food engineering researchers in Iceland with regard to this development and what strategic aim Matis ohf and the University of Iceland will take to ensure their competitiveness in this fast developing area.

Introduction

Food is a complex phenomena and the food market mirrors this. It is therefore admittedly a simplification, as is done in here, to divide the food market into three segments: low value (low cost), intermediate and high value. This approach is however widely accepted. Living standard in Iceland is high, salaries are high and production cost is generally high. Consequently, the high value food market is the most appealing one to Icelandic food producers. Because of this, and the fact that the high value food market is rapidly growing, the focus of this article is on the trends in food engineering that apply mostly to producers aiming for the high value end of the market.

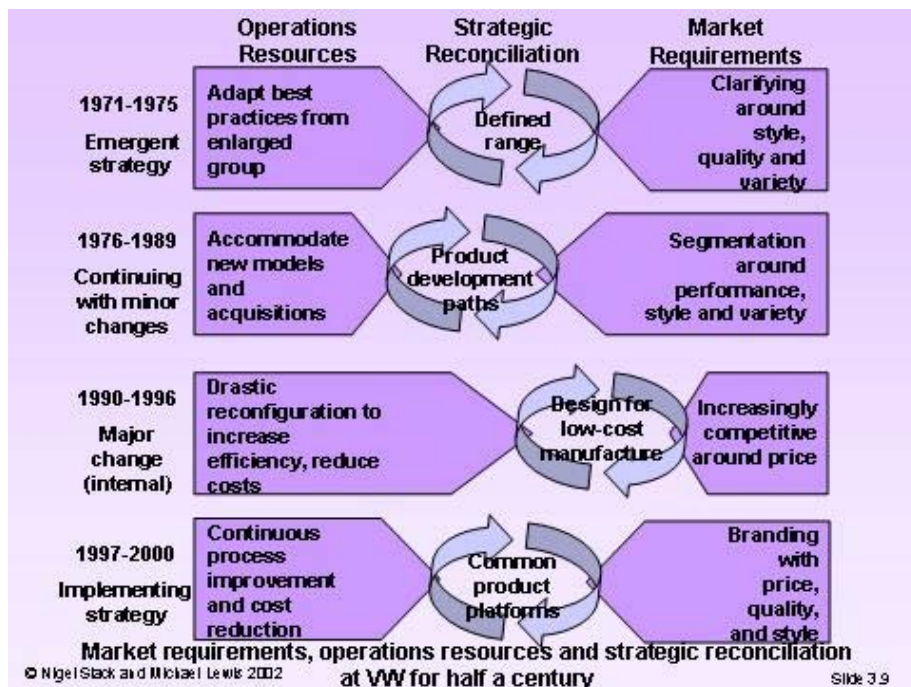


Figure 1. Market requirements, operations resources and strategic reconciliation at VW (Volkswagen) from 1970-2000.

Consumer behaviour has changed considerably over the last 60 years. The post-war shortage was solved with increased capacity in production and simplicity of products. Since then, prosperity has increased which has meant more focus on differentiation in one way or another. Today, it is not enough to be able to produce, you must be able to produce something *different*, but also a great quality and cost-competitive product. Figure 1 (Slack and Lewis, 2002) shows how this change in market requirements changed the operations strategy of the car producer Volkswagen from 1970-2000. It is evident from the figure that the weight of cost efficiency, quality and style increased greatly in the last part of the 20th century.

The same market requirement applies to food market requirements. The nature of the food market, as well as development over the last few years has also placed more burden on the shoulders of food producers. Firstly, consumers are concerned about their safety and well-being due to recent unprecedented food scares, as well as positive and negative news on the effects of food on health. Secondly, consumers are concerned about the environment – sustainability is playing an increasingly critical role in marketing of food products. This can e.g. be seen in extended demands for eco-labelled food products. Thirdly, consumers are becoming more and more aware of their power to influence communal development with their purchasing power. The concept of ‘fair-trading’ (i.e. buying food which is grown, harvested and processed in such a way that ‘fair’ distribution of the profits made in a supply chain between the links in the chain is ensured) is gaining momentum. The vision of ‘fair-trade’ is stimulating development of farmers and other raw material suppliers’ societies. Summing all this up gives the keyword: solicitude – for yourself, the environment and the society.

Consumers of the 21st century are well informed. The internet provides consumers with access to information on more or less everything they like to know, including health effects of food ingredients and other information affecting consumption. The level of education has, and will be growing and consumers are used to ‘filter out’ information they find credible and information they find not. This puts pressure on the quality of information delivered with food products – it has to be comprehensive, simple and still be put forth in such a way that consumers find it credible.

The food supply chain has changed greatly over the last two decades. Firstly, growth and merging of retailers has created multi-national companies selling a large part of their wares under their own label. Stiff competition between retailers and profitability demands of share holders put pressure on producers with regard to price. At the same time, quality demands of the retailer are increasing, since quality defects on a retailer labelled product will not only spoil the reputation of the product itself, but the retailer brand as a whole. Secondly, speciality stores (e.g. focusing on ecology, organic food or kosher food) have flourished. These stores (or chains of stores) often request different characteristics of the food products. Style and differentiation is the keyword here. Consumers (especially those willing to pay a little extra for their products) are tired of homogeneity and standardisation – they demand a different *experience when enjoying* their food.

This development puts both food producers and R&D institutions in the food industry in a difficult, but exciting situation. A decision must be taken: – where shall the focus be? Is it wise to focus wide or narrow? This will not be answered for food producers here, but in our opinion the answer for Icelandic food research is: both! There is a need for specialisation but maintaining overview is also vital. This calls for the same development in R&D as in retailing, i.e. the merging of institutions. In the following chapter a few topics concerning

trends in food engineering will be addressed and clarified how and why we find those topics interesting.

Fresh Products, Cooling Instead of Freezing – Superchilling

Even though freezing has not been shown to be exchangeable as a necessary method when it comes to preserving food products, the importance of freezing, compared to chilling, has decreased much for the Icelandic food industry in the last decade. It is estimated that of approximately five billion tons of produced food worldwide, some two billion need refrigerated processing (Fikiin, 2003). Worldwide, only 400 million tons out of those five billion get sufficient refrigeration, but in Iceland the situation is different. Icelandic consumers and consumers in Western Europe (the most important market for Icelandic food products) are loosing interest in frozen food – they want the food to be fresh. The fact that Icelandic food production takes place relatively close to the market (at least compared to low-cost producers such as China, Vietnam and other countries in Asia), also gives the opportunity to export the products without ever having to freeze them. Figure 2 shows the development in this for three of the most important groundfish species caught and processed in Iceland.

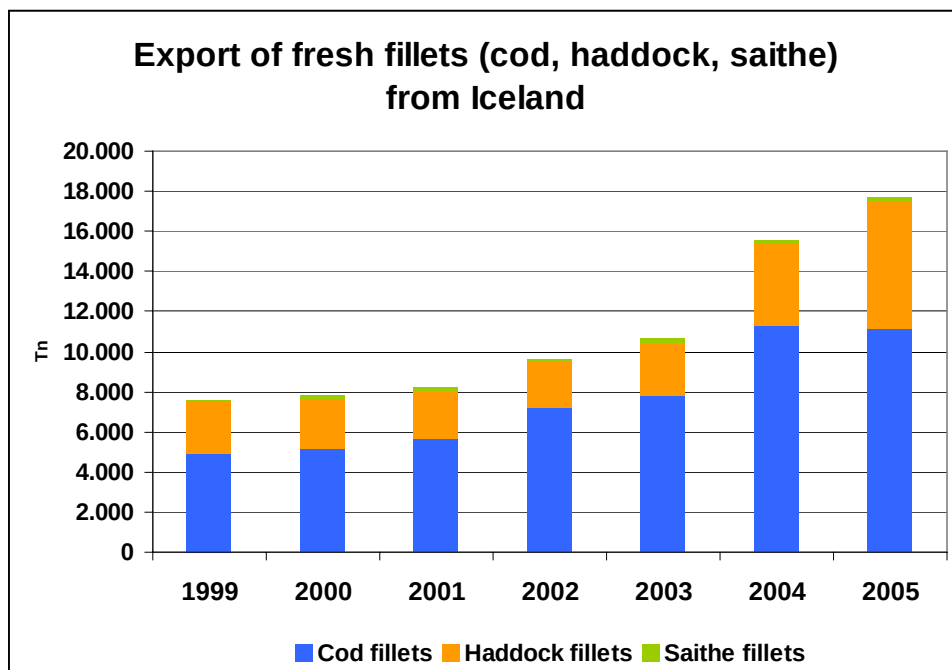


Figure 2. Export of fresh fillets from Iceland (Arason, S. 2007).

Leaving out the operation unit of freezing puts more pressure on the value chain in terms of quality and spoilage of the products. Enzymes and micro-organism is “disabled” during the freezing state, but chilling only slows the degrading processes of enzymes and micro-organisms down. Because of this, the largest proportion of the increase in fresh products

from Iceland has been transported with air cargo. Air transportation is substantially more expensive than sea transportation (land based transportation is not a feasible option from Iceland!) and creates more negative environmental effects – which is not good in times of CO₂-miles and sustainability discussion. The Icelandic food industry, highly dependent on export, has therefore been putting much effort into increasing the shelf life of fresh products, in order to enable sea transportation. One promising method to do this is superchilling. Superchilling is based on chilling the products below 0°C and therefore partially freezing the water contained in the products, but still doing it in such a gentle way that the physical changes that occur when freezing do not occur. One experiment, carried out at Matis ohf, revealed that when fillets of Arctic charr (*Salvelinus alpinus*) were packed with dry ice or ice packs and stored chilled (3-4°C) and superchilled (-2°C), the shelf life was 6 days longer for the superchilled fillets, in comparison with chilled fillets (Bao, H.N.D. Thorarinsdottir, K. and Arason, S. 2004). No negative effects on the quality of the fillets were observed. Consequently, superchilling enables transportation of a higher quality Arctic charr fillets to distant markets by using sea freight instead of air freight. In another study at Matis, the effects of combined application of MAP and superchilled storage on the shelf-life extension of fresh cod loins were studied. The influence of MA packaging (50.0 % CO₂-45.0% N₂ -5% O₂) and storage temperature (1.5°C or -1°C) to prolong the shelf-life of cod loins was evaluated by sensory analysis (Quality Index Method (QIM) and Quantitative Descriptive Analysis (QDA)), physical, chemical method and microbial analysis. Compared with traditional chilled storage in polystyrene boxes (1.5°C), MA packaging and superchilled storage alone increased the shelf-life of cod loins from an average of 9 to 14 days to 16-17 days. When combined, a synergistic effect was observed and the shelf-life might be extended further, to at least 24 days (Martinsdottir, E., Magnússon, H. and Sveinsdottir, K., 2005). This is uniform with Sivertsvik et al (2002), who found a typical shelf-life extension of about 7 days is obtained for superchilled MAP fish in comparison with traditionally stored fish on ice of the same type. An acceptable sensory shelf-life of 21 days was observed for mackerel at -2°C in 100% CO₂ (Hong *et al.* 1996). For smoked blue cod, an extension of shelf-life by half was gained when the storage temperature was decreased from 3 to -1.5°C (Penney *et al.* 1994). All these studies indicate that using MA packaging, along with superchilling will enable producers to increase shelf life of fresh products considerably and thereby, increasing the ratio of fresh products that is exported via sea freight instead of the more environmentally and economically expensive air freight.

The growth of the chilled food market will continue to affect Icelandic food production. One Icelandic company, Bakkavor, has gained a considerable market share on one of the most advanced food markets in Europe, in the UK, and has been expanding the market area over the last years. Bakkavor, which started as a small company, only producing from Icelandic raw material, is typical for the present development in Icelandic food industry. The seafood companies, many of which have management teams with international experience, have been buying up processing factories closer to the market areas and this will continue. Other principles apply to the other food production sectors. The meat, dairy and other food production industries have been heavily protected in Iceland over the last decades. A more pragmatic approach and pressure on food prices will most likely diminish this protection (e.g. increased import will be permitted). This could mean that some producers will have to look more carefully at niche markets. The Icelandic lamb might be a good candidate to succeed in niche markets – the uniqueness of Icelandic nature, combined with long tradition

of “non-industrial” breeding of the Icelandic sheep stock may well turn out to be an important market tool for Icelandic farmers in the future. This will, however, put more pressure on the lamb meat value chains to using this uniqueness strategically and not to let short term interests get in the way.

Evaluation of Raw Material

The evaluation of raw material, before processing, is of utmost importance in Icelandic food industry today. The “good old” days of being able to sell everything (at the same price) will not return. Differentiation on the market and the protection of good reputation are much too valuable factors to spend them by using all raw material in the same way, regardless of the customers’ demands and wishes. Since raw material for food production is a complex matter, with spatial, seasonal and other variations, it is important to be able to evaluate the status of the raw material at the time of processing. Here, as generally in the Icelandic food industry, the main focus is on the methods for evaluating the quality and condition of fish. Two panel methods, QIM and QDA have been used for the evaluation of the characteristics of fish as a raw material. Both methods have the disadvantage of being very labour intensive and requiring fairly well trained staff in order to carry them through properly. Some physical and chemical measurements, such as pH, Total volatile basic nitrogen (TVB-N) and trimethylamine (TMA), along with microbiological analysis have also been used. All of the aforementioned methods have their disadvantages: pH not being very informative and TVB-N, TMA and microbiological analysis being both labour and time consuming and not feasible for a fast conveyor belt production. A new method, currently being evaluated and studied quite extensively at Matis, is Nuclear Magnetic Resonance (NMR). Nuclear Magnetic Resonance (NMR) has become one of the most important analytical tools in a wide range of fields because of its many applications, high efficiency and accuracy. Despite of its many applications and possibilities NMR has not been used before in food research in Iceland.

Low-field NMR (LF-NMR) has been shown to be a fast and accurate method in comparison to chemical methods for measuring total moisture, fat etc. in samples (Ablett, 1992; Gambhir, 1992; Sørland et al., 2004 etc.). No solvents are used in the sample preparation, and therefore NMR measurements do not spoil the samples. NMR can therefore be a good online measuring device on a production line, simplifying process control, e.g. of the water content or state of water in fish or meat in processes such as drying, freezing or salting. The use of Magnetic Resonance Imaging (MRI) techniques are more commonly used in such measurements (Hills, 1995). This has to do with the advantage of being able to view the spatial distribution of substances in two or three dimensions with MRI.

Because of its sample non-destruction, MRI can even be used to measure water and fat content in in-vivo samples (Martinez et al., 2003; Bock et al., 2002 etc.).

Low-field Nuclear Magnetic Resonance (LF-NMR) has been used at Matis to evaluate the quality and quantity of water in fresh cod mince and to study the effects of salt content on the water properties and freezing process of cod mince (Guðjónsdóttir, M, 2006). Projects, in cooperation with food equipment producers such as Marel are being prearranged at the present at Matis ohf. The possible outcome of such projects, an online measuring device, capable of revealing the spatial distribution of water and other important substances in raw material in food production, will increase the water management abilities of food processing

substantially. Along with brining and/or injection of water, it will enable more standardized processing of food products and better utilisation of the raw material.

Improved Use of by-Products

The utilisation of by-products in the Icelandic fish industry has been growing rapidly during the last decade. Until recently, by-products were not regarded as “by-products”, but more as offscourings – the raw material that is left when other products have been produced. Here, for the sake of simplicity, we will use by-products.

By-products in the milk industry are used in the same way in Iceland as in many other countries, with one important deviation which is the Icelandic product *skyr*. Skyr is produced from whey and has been produced in Iceland for hundreds of years. Recently, export of skyr started in the sense that the formula for making skyr has been sold to Denmark (a kind of franchising) and more countries are now being considered as possible markets for skyr. The utilisation of by-products in the meat industry is not at a high level and therefore our main focus here will be on the seafood industry.

Fishmeal and -oil constitute the bulk of the volume of products from fisheries in Iceland, typically 60-70% of the total volume. The value is however far less or only 10-15% of the total value of exported seafood products. Since both the fishing fleet and the processing plants in Iceland are highly mechanized (and therefore a large portion of the running cost is financing cost but not labour cost), it is important to utilise the raw material as effectively as possible in order for the fishing industry to thrive. It has therefore, for quite some time been a goal for the fishing industry to, on the one hand to increase the percentage of processed seafood which can be processed for human consumption and, on the other hand, to increase the proportion of the catch that is processed in one way or another, instead of being discarded. As an example, all cod heads from land-based processing plants are now being utilised and many of the freezer trawlers freeze the heads of the cod for further processing onshore. In general, the utilisation of land-based processing is still much better than the utilisation of sea-based processing.

Figure 3 shows approximately how the mass flow is in cod catch and processing.

As is apparent from figure 3, more than half of the weight of the initial raw material is not used for the main product. Therefore, utilisation of by-products greatly influences how good the total utilisation of the raw material is. With higher quota prices in recent years the price of raw material has increased. High raw material price has thus been an impetus to utilise the raw material better in order to maintain profitability.

Viscera (including liver and roe) constitute between 10-25% of the net weight of fish. It is a common procedure to discard viscera in Iceland, partly because of the fact that it is obligatory to gut all fish that is to wait more than 24 hours until processing. Higher prices of roe and other by-products have however encouraged the exploitation of at least the roe from most of the harvested demersal species. This has enabled the production of products from fish viscera, such as Penzyme, a proteinase from cod which is currently being sold in Iceland and abroad as an enzyme ointment. Hydrolytic enzymes are used widely in industry, medicine and research and therefore there are opportunities for further development in this area.

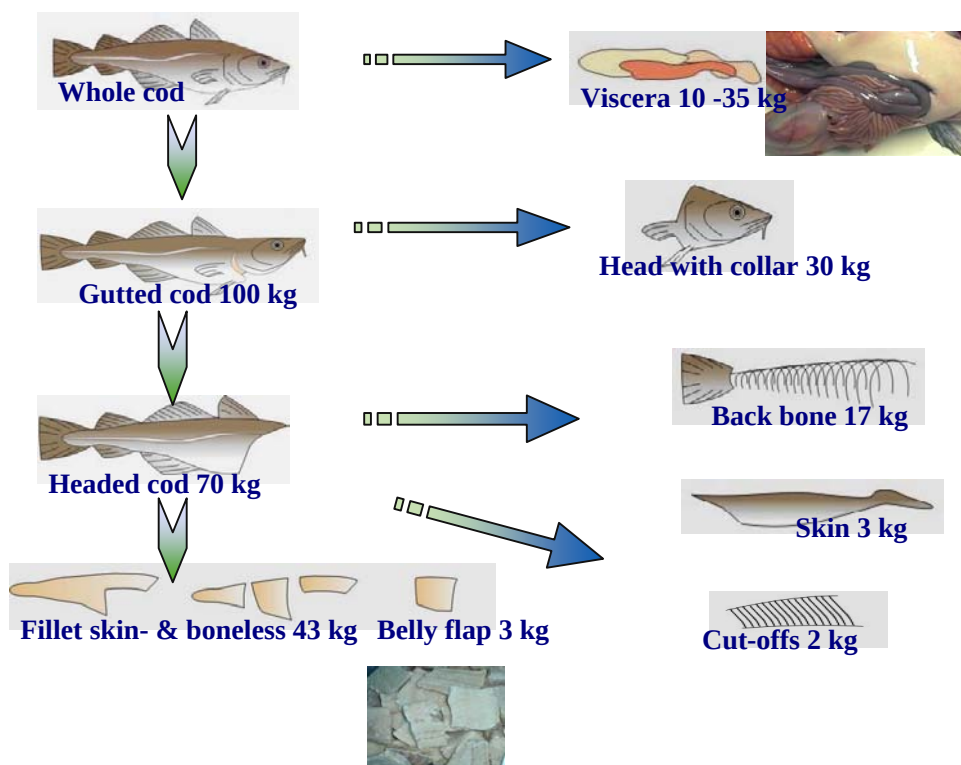


Figure 3. Products and by-products in cod processing.

A well-known Icelandic fish by-product is called Lysi, or cod liver oil. The high amount of omega-3 oil in the liver makes it quite valuable and, occasionally demand can not be fulfilled with the amount of cod livers coming onshore today.

Cod roe are another well-known Icelandic fish-by product. There is a high demand for frozen and salted cod roe for smoking, canning and in the production of different kinds of spreads. Roe from other demersal species are used in a similar way. Lumpfish and capelin roe are also valuable and are utilised.

A considerable amount of fish flesh from demersal fish can be collected from the collars and frames after filleting. This flesh may be used in mince production, but in Iceland this has not been widely practised. The mince production in Iceland is based on cut-offs rendered by the production of boneless fillets. An increased use of the flesh from the collars and frames is very important for the Icelandic fish industry, since it is considered likely that up to 15-18% of the weight of gutted cod may be actual raw material for mince production (from cut-offs, collars, heads, belly flaps and frames). Recent experiments with hydrolysates production from the flesh have been satisfactory and may be the way that the industry will be working in the future.

Fish skin has been used both for gelatine production and leather, but much attention has not been given however to research and development in that area. More attention has been given to drying of fish heads, which is being done in special drying-plants in Iceland. Cheap, geothermal energy is being used for the controlled, mostly mechanical drying process, allowing the production of high quality dried fish heads.

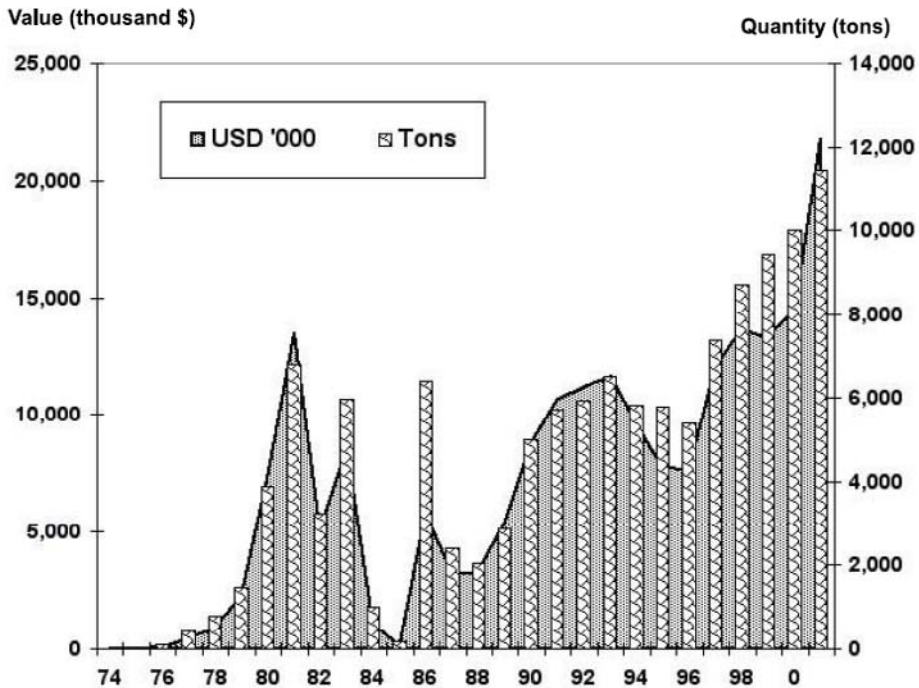


Figure 4. Quantity and value of exported cod-head products from Iceland, 1979-2001.

Shrimp offal, which constitutes about 50% of the shrimp, contains proteins, chiting and astaxanthin. All of those characteristics make shrimp offal a feasible choice for utilisation and as a matter of fact, there are already two companies producing shrimpmeal in Iceland. Another, more “cutting edge” processing of shrimp offal is the production of chitosan, a biodegradable product polysaccharide with application potential ranging from cosmetics to medical applications (Sikorski et.al 1995).

It is expected that the use of geothermal energy will increase in processing of by-products and even fishmeal production in the future. The price of oil has risen sharply in the last decade and since much geothermal energy is available in Iceland the use of it looks encouraging under such circumstances.

It is known that discard of fish and offals from fish processing is considerable. The utilisation of this “waste” is driven by economic factors and it is therefore important to increase knowledge of by-products in general, in terms of seasonal and spatial variation, in terms of market potential and in terms of processes for preservation and utilization. In order to do this, we consider it necessary to record in a structured way the characteristics of the by-products and to develop systems to sort and handle them on board fishing ships. Cost-effective preservation methods and improved logistics from vessels to processing plants are also of great importance.

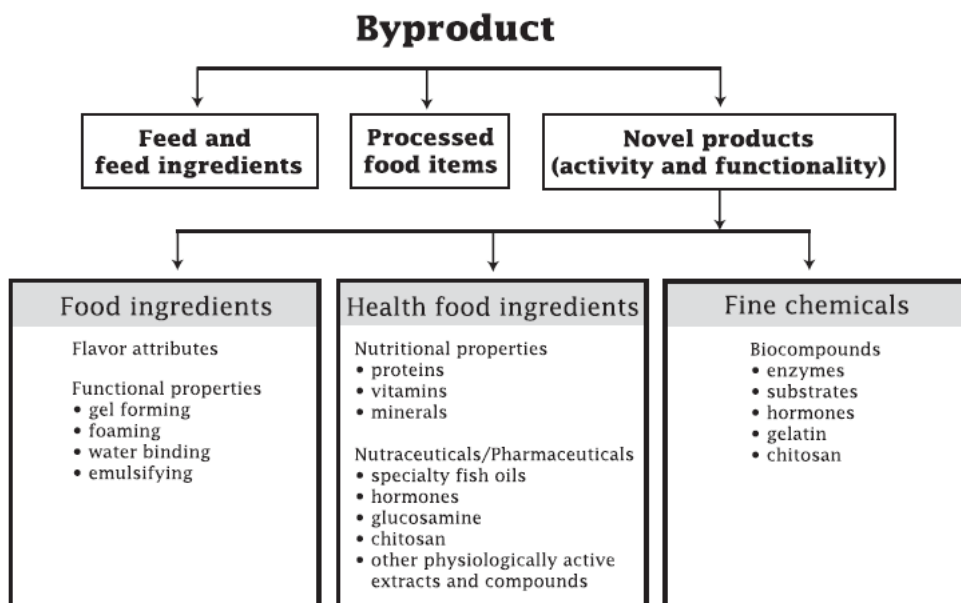


Figure 5. There are many interesting possibilities for byproducts from fish.

Low Energy Use in Production

The cost of energy has been rising over the last few years. The price of oil has risen sharply and the environmental cost of energy use has become ever more evident as the greenhouse effects gain more and more attention. This has led managers in the food value chain, to search for possible ways of decreasing the dependency of expensive and environmentally unfriendly energy. In Iceland this has been evident in the development of greenhouses where the geothermal energy is used for heating, as well as development in other sectors of the food industry, such as drying of fish heads.

However, it is a well-known fact that the largest single entity of oil (and therefore producer of CO₂) in the food production industry in Iceland is the fishing fleet. Björnsson et al (2004) found out that between 27-35% of the total use of oil in Iceland from 1986-1992 was because of the fishing fleet. Therefore, a substantial effort has been put in decreasing the oil use of the fishing fleet. During a typical fishing trip, 1-4 types of fishing gears are used, 1-2 or more fish species are caught and the fishing gears are operated at different water depth. The single most important factor, as far as the fuel consumption is concerned, is the fishing gear, which is responsible for more than 70% of the fuel consumption of the fishing vessel when fishing with bottom trawl. The relative energy use for different operations of a fish processing trawler during fishing with bottom trawl can be seen in Figure 6 (Yngvadottir et al, 2003).

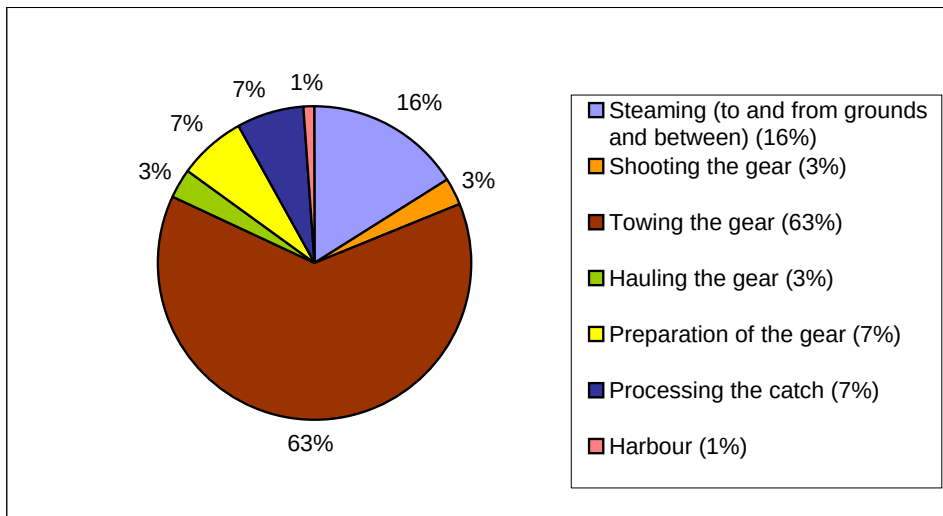


Figure 6 Relative energy use for different operation in processing trawler during fishing with bottom trawl.

When it comes to processing, electricity is the most widely used source of energy. Figure 7 shows the distribution of the used energy in a typical processing plant. It is evident that freezing is the single most important factor on energy use in processing. This may however have changed slightly in the last few years, following the increase in processing of chilled products.

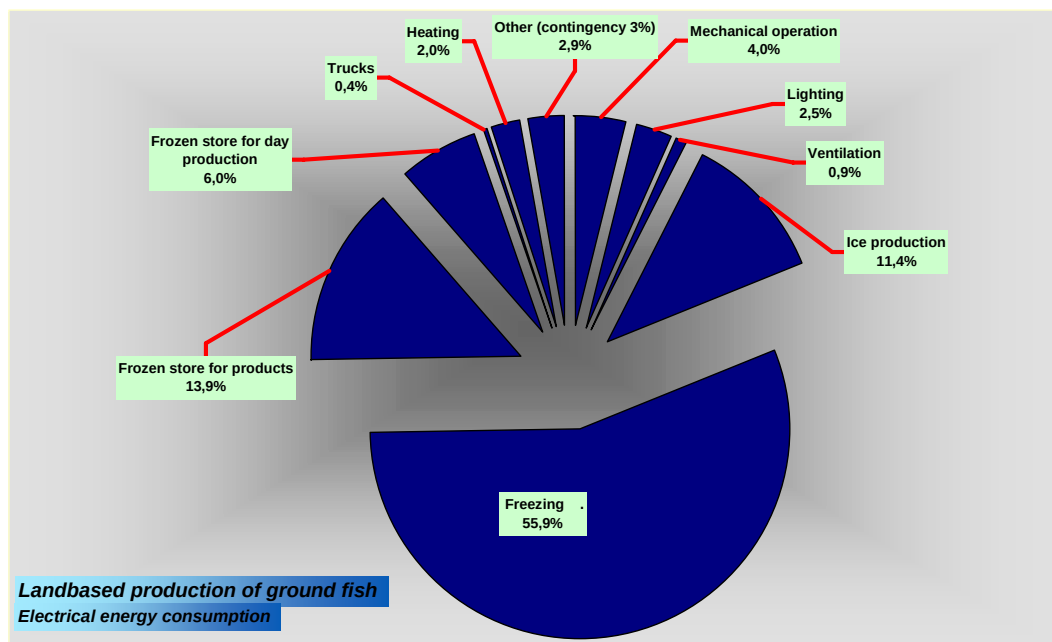


Figure 7. Relative energy use for different operation in a filleting, freezing plant.

Much more emphasis has been put on decreasing the energy used by the fishing fleet rather than the processing plants. This is probably due to the fact that the price of oil has risen much more sharply than the price of electricity in Iceland and the fishing fleet is therefore spending more on energy than the processing sector, proportionally to the total cost in each instance.

The choice of a fishing method is important when it comes to the use of oil in fisheries. Trawling is a common way of catching demersal fish in Iceland. It is known that the resistance of the trawl net increases as the trawl wears. This increase is thought to be up to 10% (Yngvadottir et. Al, 2003). It is therefore important to use new trawls. Research projects, with the aim of finding the right time to change trawls seem logical for the Icelandic fish industry in the future.

Value Chain Management, Including Optimisation of Transportation

The concept of the value chain has been increasingly used in the Icelandic food industry in the last years. A research project which has been carried through at Matis, called *Processing forecast of cod* (Margeirsson et. al, 2006a, Margeirsson et. al, 2006b and Margeirsson et.al. 2007), has changed the way managers in the seafood industry consider data gathered during catching and processing and has increased the demand for research for helping management in seafood companies. The fact that the same party often owns Icelandic fishing vessels, fish processing companies and marketing companies has also increased the generic thinking in the industry, trying to maximize the profits of the total chain from catch to consumer instead of only looking at an isolated link in the value chain. It is now possible to estimate properties of catch, based on historical data and to evaluate long sailing times and value of catch, since it has been shown that the properties of the catch (and hence the value of it) is both spatially and temporally dependent. Increased use of automatic data capturing methods, such as electronic log-books and weighing machines onboard the vessels have also enabled better inventory management, based on the age and size of the raw material and other factors considered useful for planning the processing. Use of RFID labelled fish tubs is also increasing rapidly, making such inventory control and traceability more automatic and precise and therefore enabling different processing for raw material with different properties.

A field study has been carried out in an Icelandic fish processing and marketing company, to study the quality management of the Icelandic fisheries industry with emphasis on the traceability system. Data relevant to the traceability of products in the company Icelandic Group were collected and compared with the TraceFish standards. The TraceFish standards are the outcome of an EU funded concerted action project "Traceability of Fish Products". The results show that the standard for captured fish is both practical and realistic for the frozen cod distribution chain in Iceland. There is no reason to believe that other kind of processing (chilled, salted etc) are doing any worse and Icelandic fish industry can therefore be considered *traceable* (Liu, 2002).

Genetic Improvements of Crops and Farmed Animals

Genetic technology has been used for the development of agricultural products such as crop for decades. The application of genetic technology has also been used for the development of farmed animals within the agricultural sector, but, until now, to a limited degree in traditional fisheries and that includes farming of fish and shellfish. The reason is mainly because it is more logical to use it for farmed animals that do have limited number of offsprings.

Traceability and marketing is an interesting subject and there is an increasing interest by the marketing end to have the possibility of being able to sell fish by using the name of the boat, and the crew. Such examples can be seen in marketing of wine where a picture of the farmer and his family is used for marketing of the wine. In doing so it is necessary to be able to verify the origin and one possibility would be to use genetic code for the fish from different areas. Marketing based on the origin is called *selling by using storytelling* and that technique can be seen for example at Wholefoods in the USA.

Marketing Food Products

Complications in marketing food products have probably never been greater than today. A thorough knowledge of the product is essential and has more effect on the marketing of food products than ever, but at the same time price awareness is a very important thing.

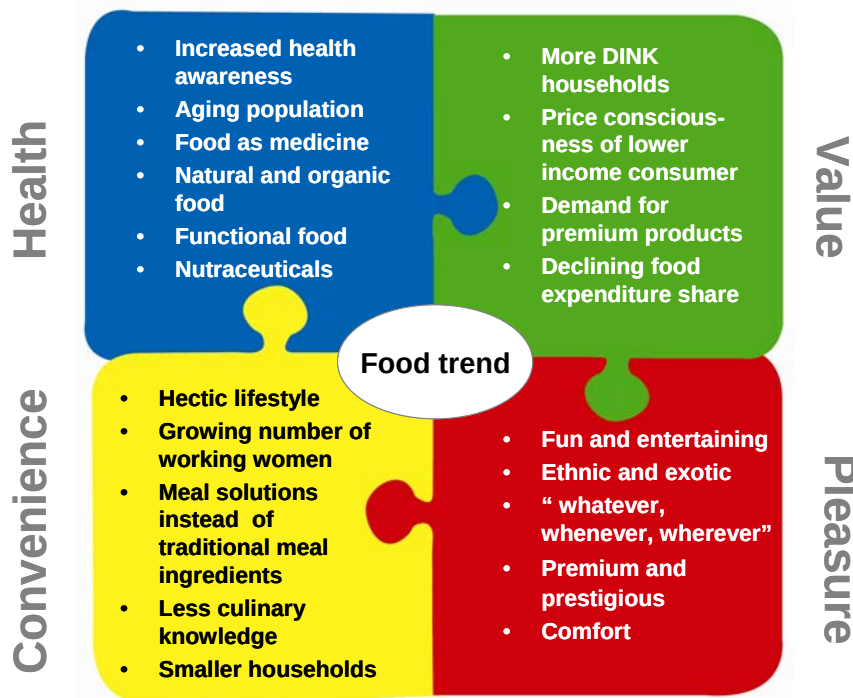


Figure 8. Factors having an effect on development of food marketing.

The keyword in marketing food products today is differentiation. The food market has been developing towards segmentation in the last decade. Discount shopping has grown substantially, but high value shopping has been booming as well. Wal-Mart, Tesco and other discount retailers have gained larger and larger market share, but at the same time speciality stores have flourished.

Consumers are today better informed than ever. European consumers have experienced food scares such as BSE and dioxin and consequently, like to know where their food comes from. Traceability is therefore a vital tool for marketing and is, in reality, a basis for being able to differentiate from other products on the market. Information on where the cattle is raised, slaughtered and the steak is cut is affecting consumer behaviour today. In some ways this contradicts the principles of globalisation, which has, to some extent at least, eliminated borders between countries. Johann Lindenberg, the chairman of Unilever states the importance of traceability in this context quite well: "In my mind there is no doubt that the importance of traceability will continue to grow. Consumers want to know where the product is coming from. If the traceability is lacking, it will be mentioned in the media and then a negative image is created" (Árnason, 2005).

Price is a key factor when consumers choose their food, but at the same time, *enjoying* food is becoming trendy. Higher household income enables people (especially those in the higher end of the income curve) to focus less on the price and focus on quality instead – at least occasionally. When we buy cereals for breakfast we go to the discount store the cereals is the same wherever we buy it anyway), but when it comes to choose lobster for the dinner on a Friday evening, we prefer quality and we like to be able to tell our guests a story and the story is about the food we are offering them. Where did the lamb on the table come from, who bred the lamb, in what part of the beautiful highlands of Iceland did it grow, was it *organically* grown and so on.

Organic and sustainable food production is a phenomenon that has developed slowly in Iceland compared to many other countries. The farming of agricultural products and the catching of fish has always been considered as being done in a responsible way. Icelanders have estimated that the food production has not affected the environment in a negative way – at least not much. This is probably right, but the growing importance of having external, independent party to certify this for the market has caused growing discussion on eco-labelling in one form or another. Eco-labelling is really a part of a much larger phenomenon: solicitude. Consumers care about their health, the health of the environment and the development of the global community (we do not like to eat products which we know are causing adverse health effects on the workers in the value chain).

It is our evaluation that environmental and solicitude issues will continue to play an increasingly important role in marketing of food products (especially those in the higher end of the price spectrum) in the future. As Jonathan Porrit, director of Forum for the Future and co-author of the report, *Fishing for Good*. Globally, puts it: "It will mean that supermarkets can display cod with the MSC logo next to cod without it, and allow customers to notice the difference," says the report. "This is exactly what happens now with Fairtrade bananas: they sit right next to standard bananas and are taking proportionally more and more of the sales." (Maitland, 2005).

Convenience is another very important factor in the marketing of food. One-third of meals in UK is cooked in less than five minutes, according to Seamus FitzPatrick, a board member of Young's Bluecrest in UK (Árnason, 2004). From an Icelandic point of view this is

in particular important in terms of seafood. It has already influenced and will continue to steer the development in Icelandic food production (seafood production in particular) towards fresh, instead of frozen products and more advanced processing (delivering a whole meal instead of only the ingredients). The effect of this will likely be more raw material export from Iceland, to production plants closer to the actual market areas.

All of the aforementioned factors will play a role in the branding of food products. Information on traceability, origin, production methods, ethical matters and how the product can ease and prolong your life are all a part of the “package” bought when a food product leaves the shelves of the store. It is no longer enough just to deliver the food – consumers want something more.

Operations Research and Food Engineering

Operations research (OR) has played an important role of food engineering in Iceland and will continue to do so. Food production means mostly fish in Iceland as mentioned earlier in the chapter. The discussion on OR here will therefore mostly take note of fisheries and fish processing. Catching the fish is the first chain in the value chain of seafood products and in many aspects the most important one, since it is impossible to make good products from bad raw material. Today, Iceland is approximately in 10. place as the biggest fishing nation in the world, with a total fish catch amounting to around 1.1 - 1.3 million tonnes and fisheries are controlled by a quota system that was introduced in the 80's. Stagnating or even decreasing quotas in the last decade has shifted the focus ever more on the importance of utilizing stocks in a sustainable way and maximize the value of the catch, especially in the case of cod, which is by far the most important species in terms of value.

Research has shown that the proper processing and handling of the fish can give great increase in value (Rúnar Birgisson and more, 1996). A link between the quality of the flesh of the cod and how the fillets can be used has been established. Factors, such as nematodes, bloodspots, bruise and gaping of the fillets are costly. Difference in the properties of cod depending on different seasons and on which fishing areas it is caught, has also been shown (Sveinn Margeirsson, 2003).

The first extensive use of OR in the Icelandic fishing industry began in 1966. This was a simulation model on catching and landing of a herring (Ólafsson 1995). In the year 1969 a similar simulation model was used to investigate fishing vessel operations; a comparison of operational profit between different trawlers was done by comparing vessels of different sizes and study the supply of raw material to freezing plants (Sigvaldason, 1969).

In 1981 Jensson presented a simulation model where the fleet and problems concerning congestion were investigated. The fleet operation, the total catch and processing were the subject of the report. Digernes (1982) looked into fishing vessel design and its influence on operation and efficiency. He used analytical approach and discussed income as a function of fishing time, tools and price for the catch. Arnason (1984) studied the feasibility of operating a trawler versus operating a long liner. Gunn, Millar and Newbolt (1991) looked into planning for Canadian company with fishing and production. An LP model was made for processing to maximize profit. Included in this was the trawler fleet, processing and the market. Andrason (1990) developed models to use in production management and production on board Icelandic trawlers. Arnason and Jensson (1991) used these models as a prototype to design simulation

model that analyzed the operation of a trawler operation. Gunn (1992) developed a two stage procedure for planning marketing and fishing activities for fish processing firms.

Wallace and S. Ólafsson (1994) did a simulation model for the Icelandic trawler fleet. It incorporated both biological and management factors for fishing and processing. The model was thought of as being a tool for management where the influence of different management techniques could be observed. The profit of the fishing company was maximized.

Helgason and Olafsson (1988) made a deterministic Decision Support System (DSS) for long time and short time fisheries management. It included type of boat, short time banning, mesh size regulation and quota. The profit and cost of the processing was also calculated. The model returned the expected catch, economic outcome and other data ten years into the future. The fleet and the recruitment were kept constant.

In 1999 an Icelandic software company put on the market a program that could be used for optimization within fisheries companies. Jensson and Gunnarsson (2000) discovered that it was difficult to estimate the economical profit of the software, but that it gave good experience in assisting with decision making. It was intended to be used when working with operation scheduling and it provided overview of the management of the company. This was the first Icelandic software where so many influence factors were included. However, this software got only a limited distribution, mainly due to a lack of data.

Guðmundsson et.al. (2006) put forth an aggregate quota allocation plan for one year. In his report, the year was divided into four seasons and the Icelandic fishing territories into 13 areas and took into account Margeirsson (2003). The plan outlines where a trawler should go to fish within the Icelandic territorial waters depending on the properties of the cod. It also outlines how much of the yearly quota should be used in each season and the product mix.

Hasan and Raffensperger (2006) introduced a daily trawler scheduling based on the catch capacity of the trawlers and the capacity of processing firms. A mixed integer linear programming model is used to co-ordinate trawler scheduling, fishing, processing and labour allocation of quota-based integrated fisheries.

Regarding coordination of fishing and processing, papers include Mikalsen and Vassdal (1979) who made a multi period LP model for one month production planning where the goal was to smooth seasonal fluctuations of fish supply. This model was market driven. Jensson (1988) optimized profit for a five days sailing plan. In his research, the production planning in fish processing plants was analyzed. The product mix and market fluctuations were determined and the stochastic nature of the catch. Randhawa and Bjarnason (1994) integrated LP and simulation to coordinate fishing and processing on a macro level. A trawler scheduling model and LP were used to decide about the catch, work, product mix and inventory. In this report, quality information about the fish were implemented. Gunn, Millar and Newbolt (1991) studied integration of fishing and fish processing and Jensson (1990) wrote about how to coordinate scheduling for the landing of trawlers and processing. Haley (1981) used OR to compare the components of a fishery to various components of the production process.

Randhawa and Bjarnason (1992) presented a relative quality function between the qualities of the raw material to its value as the catch ages while the trawler is at sea fishing. This function was developed based on information from (Hauss, 1988).

Rúnar Birgisson et.al., 1996 showed how proper processing and handling of the fish increases its value. A link between the flesh of the cod and how the fillets can be used has been established. The use of the fillets is very important when it comes to profitability of the

cod. Factors such as nematodes, bloodspots, bruise and gaping of the fillets are costly. Difference in the properties of cod depending on the season and on which fishing areas it is caught on has also been shown (Margeirsson et.al, 2007).

As can be seen from above, fishermen, processors, distributors and managers can all influence the quality of the fish. This fact has resulted in an ongoing project for optimizing and analysing the seafood industry in Iceland. The project is twofold. The first part of the project focuses on gathering historical data and combining the data into a centralized research database. Each participating seafood company in the project has a local database which is used to gather data for statistical analysis and to estimate input parameters for the optimization model. All participants in the project can share their data with other participants or keep their own data separate. Each participant shares data with a research database at Matis ohf and this centralized database will be used for research purposes.

The second part of the project is a linear optimization model that maximizes the revenue of a fishing company. The model uses the historical data gathered from leading Icelandic seafood companies to determine the optimal fishing grounds, the ideal expected catch and the best processing methods for the catch over a time period, while maximizing the overall revenue of the fishing company. The optimization model includes both detailed routing of the fishing fleet and the allocation of the catch, whether to sell the catch directly on the market or to process it. The model also selects which products the processing should focus on, based on the expected available material. We use historical data for each fishing ground and for each time of the year to estimate the quantity of each fish species which the ships are expected to catch in a specific fishing ground at a specific time of the year.

As far as we know, attempts to connect the location and time of year of the fishing fleet and the expected catch with the revenue of a fishing company has not been done before. This is also the first time that leading Icelandic seafood companies combine their forces to create a detailed centralized database of the fishing grounds and the fish processing. This database will be used for research purposes, while each participant can also use the historical data for statistical analysis and to optimize planning.

Much less has been done in applying Operations Research in agriculture in Iceland than in fisheries, which is normal considering the difference in economic importance. The first study is described in Jensson et al (1978) where the concern is to plan with Linear Programming the transport of hay reserves between regions in Iceland in case catastrophes such as volcanic eruptions. Another LP model was developed during this period to aid dairy farmers in coping with milk quotas, see Jensson et al (1980). The model includes the stock and decisions on the number of milking cows, the fertilizing and hay cutting decisions and the use of other feed. A computer program based on this was developed and used by agricultural consultants during the first years of the milk quota system.

Planning the harvesting in salmon aquaculture with Mixed Integer Linear Programming is the subject of Jensson (1997). The model is market-based since it uses a forecast of seasonal fluctuations of salmon prices for different sizes of fish and schedules the graded harvest of the cages to maximize the profit of the production.

When it comes to agricultural processing, two references can be mentioned. In Jensson (1999) the location of milk processing facilities in Iceland is optimized as well as the logistics of milk from farmers to processing facilities and of dairy products to markets. This model was used extensively for policy planning in the Icelandic dairy industry.

In L ndal (2005) the use of Operations Research and statistical analysis in lamb meat production is studied, including a simulation model of the lamb slaughtering and meat processing lines.

New Methods for Data Analysis

The application of Bayesian statistics to various fields has grown dramatically over the last two decades mainly due to advances in computational methods and increased computational power. Fields such as epidemiology, genetics, environmental sciences and fisheries sciences, to name but a few, have incorporated the Bayesian approach, resulting in methods that can handle the complex data from these fields.

The Bayesian approach is based on Bayes' theorem which states how the probability of an event can be computed when conditioned on the occurrence of another event. The usual statistical set up of data and unknown parameters is approached by handling the unknown parameters as random variables while the data are assumed to be a realization from a probability model conditioned on the parameters. The application of Bayes' theorem results in probability statements about the unknown parameters conditioned on the observed data. In the Bayesian context, probability describes degree of belief but cannot be interpreted as limiting frequencies as in classical (frequentist) statistical methods.

Prior beliefs about possible values of unknown parameters need to be specified beforehand through a distribution called the prior distribution. Once the data are observed the prior distribution is updated with Bayes' theorem resulting in a distribution called the posterior distribution, which describes beliefs about the parameters after seeing the data. Knowledge about certain parameters which is based on previous measurements and findings can be taken into account through the prior distribution. Likewise, the lack of prior knowledge about given parameter would be reflected in the prior distribution.

All statistical inference is based on the posterior distribution in the Bayesian framework. The mean or the median of the marginal posterior distribution of a given parameter are commonly used as point estimates for the parameter. Marginal probability intervals or regions based on the posterior distribution are presented for similar purposes as the usual confidence intervals or regions, even though the interpretation is not the same. In most cases analytical results are not available and computational methods such Markov chain Monte Carlo are needed to evaluate the posterior distribution.

Often complex processes lie behind the collected data. A natural approach to these kind of data is Bayesian hierarchical modeling. The Bayesian hierarchical framework makes it easy to incorporate several data sources and to break down the underlying processes behind the data into connected layers. A simple, yet a typical form of a Bayesian hierarchical model, is a three level model. At the first level, the probability distribution which describes how the data were generated, conditioned on unknown parameters, is specified. At the second level, the probability model of the process, which generated the parameters in the first level, is given. This probability model is conditioned on so-called hyperparameters. This probability model could possibly incorporate physical knowledge about the process which lies behind the observed data, explanatory variables may enter at this level, and temporal or spatial processes may be used in modeling at the second level. At the third level, prior distributions for the hyperparameters in the second level are specified. Models with a higher number of levels

usually involve expanding on the second level described above. Gelman et al. (2004) give a very good overview of analysis of data with the Bayesian approach.

Food engineering should be no exception to other fields in taking full advantage of the Bayesian approach. The collection of complex data in food engineering calls for advanced statistical methods. An example of the Bayesian approach in food engineering can be found in Pouillot et al. (2003) where the risk due to bacterial growth is assessed. Pouillot et al. (2003) found the Bayesian approach useful in separating process variability and uncertainty in model parameters. Margeirsson et al. (2006) describe data on fillet yield, gaping, bruises and parasites in cod in Icelandic waters and analyze how these variables are affected by catching and processing factors, as well as spatial and seasonal factors. Further modeling of these data has led to more complex models than presented in Margeirsson et al. (2006). These models take the spatial effect into account at the finest scale of squares and a temporal effect is modeled on a monthly scale, leading to improved adjustment to the data. In case of fillet yield, a linear mixed model is used, where the catching and processing factors enter the model as fixed effects, while the seasonal, spatial and temporal effects enter the model as random effects. Line boats and trawl boats enter the model as two separate random effects as well. Further, a *t*-distribution appears to give a much better fit to the remaining error terms than a normal distribution. The inclusion of a *t*-distribution instead of a normal distribution is relatively easy in the Bayesian framework.

For count variables measuring gaping, bruises and parasites, a generalized linear mixed model involving the Poisson distribution is needed. Here, the logarithm of the parameter in the Poisson distribution is modeled with a linear mixed model which is of the same form as the model for fillet yield. In the models for fillet yield and the count variables, the effects of continuous variables is modeled with nonparametric regression. So, instead of a linear term βx , where x is a continuous variable, a continuous function $f(x)$ is used. The function $f(x)$ is approximated with a piecewise cubic polynomial. As in case of the *t*-distribution, estimation of the function $f(x)$ is relatively easy in the Bayesian framework.

This example shows that analysis of data collected in food engineering applications can require state of the art statistical methods such as Bayesian hierarchical modeling. The modeling approach described above may not only apply to fish processing data, but can potentially be adjusted for analysis of data on processing of other food products such as poultry meat and beef.

The Challenge of Tomorrow - Cooperation between Industry, Universities and Research Institutes

There is a general demand for increased information flow from the research community. The research community in Iceland, as well as in many other countries, consists of institutions, specialised companies and universities. The merging of small institutes into larger institutes, as well as merging of smaller universities has been pronounced in Iceland over the last few years. In January 2007, three different food research institutes merged into Matis ohf – Icelandic food research. Matis ohf is supposed to serve the food industry and increase value of food production in Iceland as well as to contribute to better public health through development towards more nutritious food products. Therefore, Matis ohf intends to work

closely with the food industry as well as with universities and other research parties, both local and abroad. In some other countries, such as Denmark, the development has been towards a different kind of merging in the research society. For example, The Danish Fisheries Research was merged with the Technical University of Denmark, with the aim of integrating knowledge and research in engineering and technology into seafood research. Most mergers are intended to improve the competitiveness of the institutes involved and there are different reasons in each country as to which kind of merging is appropriate. Our evaluation is that by combining all food research into one organisation, such as Matis ohf, the following advantages will be obtained:

- By having all research in all food sectors hosted at the same organisation, synergy is acquired.
- Close cooperation with both universities and industry improves the flow of information between the industry and basic research carried through at the universities. Matis ohf will be able to pick up knowledge from both the industry and universities and bridge the gap between research at the university level and the food industry.
- Collaboration on applied research projects and service delivered by Matis ohf will help the universities to “develop ideas to products,” beneficial to the food industry.
- MSc. and PhD students get opportunities to conduct real research projects at Matis ohf, but still in close cooperation with the food industry. The time consuming process of defining and running projects is managed by a specialised organisation instead of taking time from core processes of industrial companies and universities, i.e. producing food products and conducting research.
- By having mutual employees (e.g. 50% at each place), even more synergies are created. This can apply both in industry – Matis ohf and university – Matis ohf.

It can though be argued that the other kind of merging, i.e. merging institutions and universities and institutions (as the case is in Denmark). The advantages of this could e.g. be simplification of management and better utilisation of equipment. The obvious disadvantage is however the risk of losing connection to the food industry.

In a workshop of the future of Nordic seafood research (Gemba innovation (2006)) the following trends were among those mentioned: nutrition, sustainability, certification, labelling and food safety. Collaboration between the research community and the seafood industry was also considered an important topic in the future if Nordic seafood research were to prosper.

Conclusion

There is a rapid development in the field of food research and food engineering. In this chapter, we have presented few of the topics that we consider among the most important ones in the future. Many more topics could have been mentioned, but – and this is actually an important subject when it comes to strategic management in food research – it is important to focus. Research groups must be large enough and within specific fields of research in order to create a critical mass to ensure skills and competences. This may sound as a simple task, but the complexity of food makes food engineering research a very complex task sometimes! It is

therefore important that research groups consist of people with various skills. Multidisciplinary approach is essential.

Small and medium sized companies will play a vital role in the development of food engineering. Small companies enable fast reactions to market changes and flexibility. The same kind of flexibility must be integrated in food engineering research.

The vast amount of data recorded in all advanced food value chains has changed research in food engineering greatly in the last decade. The price of acquiring data has descended because of this and new methods in analysis have improved the flexibility of doing the analysis of large, but sometimes imperfect data sets acquired directly from the industry. This development will continue and be one of the drivers of food engineering research in the future. Consumers want information on their food products and by using and connecting different data recording devices in the value chain their demands can be fulfilled. It is our evaluation that Icelandic food research is particularly well prepared for this development, because of high stage of technical development in Iceland, former experience with projects of this kind and good cooperation with companies in raw material acquirement, processing, transport and marketing as well as software providers and processing machines developers. We do therefore look forward to taking part and shaping the future development in the knowledge industry of tomorrow – the food industry.

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Chapter 2

WATER FOOD INTERACTION: AVAILABILITY AND MOBILITY OF WATER RELATED TO QUALITY OF FOOD

A. Derossi and C. Severini

Department of Food Science – University of Foggia,
via Napoli, 25 – 71100 Foggia (Italy)

Abstract

Water is the most important compound of food. It affects chemical reactions, microbial growth and organoleptic quality. Historically, the effects of water on food degradation have been related to its availability but the lack of exact definition of this term has caused contradictory results. Nevertheless, it is well known that through the control of “free” and “bound” water content it is possible to restrict degradation reactions and to improve food quality.

Nowadays different parameters to measure the state of water in food are available but, from industrial point of view, the most important is the water activity (a_w). This term is used to indicate the ratio of the vapour pressure in equilibrium with a food and the vapour pressure of water at the same temperature and pressure. With the recognition of the importance of this parameter, new knowledge and understanding of water-food interaction have led to new methods to obtain shelf-stable food by reduction of water activity. Moreover, the importance of water activity led food scientists to study mathematical models to predict a_w values in complex food.

In this chapter we present results about osmodehydration and direct addition of humectants as treatments to reduce water activity in food. We studied, in particular: i) the interactions of different humectants, the influence of process variables and the development of mathematical models to predict a_w values from a statistical and engineering point of view; ii) the optimization of processes with the aim to obtain safe vegetable food with good organoleptic quality. Also, we reviewed the new water-food interaction theories based on dynamic rather than thermodynamic. In particular, we analyze the glassy transition temperature and translational diffusion coefficients measured by DSC and NMR techniques and present some preliminary results obtained on apple osmodehydrated samples.

1. Introduction

Water in biological tissues, as the most important component, plays the main role concerning the microbiological safety, chemical reactions, organoleptic characteristics, nutritional value, heat and mass transfer. Microbiologists were the first scientists that recognized the importance of the state of water rather than its content in food. On the base of this concept several terms like “free” and “bound” water, “unfreezable”, “structured”, “rotational” were used meaning the different availability of water in food.

Scott [1,2,3] defined water activity (a_w) that means how much water is available for chemical and biochemical reactions and microbial growth. Water activity is based on thermodynamic and it is used to indicate the state of equilibrium between the vapour pressure of atmosphere surrounding food and the vapour pressure of pure water at the same temperature and pressure. Starting from a_w definition, several scientific papers and books, concerning the effects of a_w values on degradation reactions of food, were published. Moreover, the recognition of the importance of a_w led the scientists to study new type of food with partial water content defined as intermediate moisture food (IMF) and new techniques to reduce a_w in food; for instance osmodehydration, humectant addition, dry infusion, moist infusion and blending. However, from industrial point of view, the success of a_w could be connected with following aspects: a) it is well correlated with microbiological growth and chemical degradation reactions; ii) it is easy to measure and results are easy to assess; iii) its measure is comparatively cheap.

For these reasons food industry have always been interested in the prediction of a_w values of food and several scientists have focused their work on empirical and theoretical mathematical models to forecast a_w values. The greater challenge concerns the application of equations, obtained from the study of model systems (i.e. aqueous solution), to complex food, like vegetable creams, meat, dairy products, etc. Chemical components of food and/or substances added to raw materials (humectants, gelling, emulsifiers, fat, ingredients, etc.) could interact among them modifying the capability to reduce a_w and this phenomena could occur also during storage time.

In this chapter we present the results concerning two different techniques to reduce a_w value. In particular we focused on direct addition of humectants on vegetable creams and osmotic dehydration with two different approaches: i) statistical and engineering, by studying the interaction of different humectants, the influence of process variables and the development of mathematical models to predict a_w values; ii) processing, with the aim to obtain safe vegetable food with good organoleptic quality. Also we reviewed the new approach based on the dynamic rather than thermodynamic theory on the state of water in food.

2. The Role of the State of Water in Food Science

2.1. Bulk and Bound Water

The term bound water is widely used in food science but it is a not easily identifiable entity, often misused and poorly understood. We should think the bound water as “*water that exists in the vicinity of solutes and other nonaqueous constituents and that exhibits properties that*”

are significantly altered from those of bulk water in the same system” [4]. In general water shows unusual characteristics compared to compounds with similar structures and molecular weights. For instance, water have unusual high melting and boiling point, it exhibits a very high surface tension, heat capacity, heat of phase transition (fusion, vaporization, sublimation) and great heat conductivity (both water and ice). All these unusual characteristics are provided from: a) the strong bound that water molecules can form among them; b) the uncommon water and ice structure. The bond angle of water (vapour state) is 104.5° ; the O-H internuclear distance is $0.96 \text{ \AA}$ and the van der Waals’ radii for oxygen and hydrogen are 1.40 and $1.2 \text{ \AA}$, respectively [4]. The electronegative oxygen, covalently tied with hydrogen atoms, produce a partial negative and positive charge on oxygen and hydrogen atoms respectively. In this condition oxygen can act as “hydrogen-bond acceptor sites” and hydrogen atoms as “hydrogen-bond donor sites”. This structure allows each water’s molecules to interact with other four molecules by hydrogen bond, thereby forming the “bulk water”. Continuous theory postulated by Bernal and Fowler [5] stated that in bulk water the structure is not completely regular but there is a continuum variability of hydrogen bond angle, energy and lengths.

On the contrary, “bound water” can be thought as a perturbed systems in which water’s molecules preferentially interact with other chemical compounds. Frank and Wen [6] showed that it is convenient to divide the layers of water in three different regions labelled A, B and C. The first one is the layer near to solute compounds, the second one is an interface region and C region represents the bulk water. In particular, A region is bound with solid compounds and it exhibits perturbed characteristics; instead, C region is too far from the solid surface to interact with chemical compounds. Strictly speaking the water’s molecules near to solid compound (region A) cannot be freely used for chemical, biological reactions and for microbial growth; in this case food may show a great stability.

However it is clear that solutes modify the water’s chemical and physical characteristics and water affects the reactivity of solutes. In particular, Marc Le Marguer [7] reviewed the types of interactions between water and different solutes (ions, apolar molecules, carbohydrates, proteins, etc.) and reported different effects defined as “structure making” and “structure breaking” on the base of the ability of chemical compounds to perturb water structure.

According to the above discussion, different levels of availability of water (the ratio between the regions A, B and C) could exist at the same time in food and the shelf life could be thought directly correlated with the state of water.

2.2. Water Activity: a Measure of the State of Water in Food

Water may influence stability and quality of food by different ways. It can act as reactant, such as in the case of hydrolysis reaction (i.e. lipid and carbohydrate hydrolysis). As solvent, water is able to decrease the reaction rate by dilution effect. Moreover, water may reduce the reactivity of chemical compounds by hydration effect on reactants (especially in the case of ions or radicals). Also, water is the most important reaction media and, if viscosity increases, reaction rate decreases due to reduction of probability of chemical compounds to collide and to react.

Taking into account all above interactions, moisture content (MC) of food cannot well explain the behaviour of degradation reactions during process or storage time.

From half the twentieth century, scientists realized that the availability of water was more important compared to its content in food. Scott [8] was the first microbiologist that defined water activity (a_w) as a measure of water availability for chemical and enzymatic reactions and microbial growth. Theoretically, a_w is defined on the base of thermodynamic by following equation :

$$\mu = \mu_0 + RT \ln \left(\frac{f}{f_0} \right) \quad (1)$$

where μ and μ_0 are respectively the chemical potential of water and of reference state usually defined as pure water; f is the fugacity of the system at given conditions and f_0 is the fugacity of the reference state [9]; T and R are the temperature and gas constant ($8.314 \text{ J K}^{-1} \text{ mol}^{-1}$) respectively. In the most practical conditions it is possible to state that:

$$\frac{f}{f_0} = \frac{p}{p_0} \quad (2)$$

and substituting into eq. 1 it is possible to obtain:

$$\mu = \mu_0 + RT \ln \left(\frac{p}{p_0} \right) \quad (3)$$

Thermodynamically, in equilibrium condition between two different phases (liquid and vapour), the chemical potential is the same in both phases, but if it is not the case, water will flow from the phase with higher chemical potential to that lower, until the equilibrium will be reached.

If the equilibrium is kept, the following equation could be used [10]:

$$\mu = \mu_0 + RT \ln a_w \quad (4)$$

where a_w is water activity.

Then, a simple correlation between a_w values of food and the equilibrium of vapour pressure surrounding atmosphere may be used:

$$a_w = \frac{p}{p_0} \quad (5)$$

a_w is also related to relative humidity, %ERH, as follows:

$$a_w = \frac{\%ERH}{100} = \frac{P}{P_0} \quad (6)$$

Also, relationships exist between a_w and colligative properties among which osmotic pressure [11]:

$$OP = -2.3026 \left(\frac{RT}{V} \right) \log a_w \quad (7)$$

Equation n.7 is very useful when the aim is to analyze the effect of a_w on microbial growth or the osmotic dehydration process. In fact, in these cases the gradient of osmotic pressure between cells and its surrounding is generally assumed as driving force of dehydration process or plasmolysis phenomena.

Nowadays a_w is the most important parameter to measure the state of water from both industrial and scientific point of view. This choice is based on several aspects:

- 1 a_w is well correlated with reaction degradation and microbial growth;
- 2 a_w is the simplest parameter to be measured;
- 3 a_w measure is fast and non-destructive analysis;
- 4 a_w measure is comparatively cheap and mathematically easy;

Despite this, a broad use of water activity to control degradation reactions and microbial growth is still far. This is because poor knowledge are available regarding the use of humectants on complex food, and the interaction between different ingredients, commonly used for food formulation, and their effects on a_w are often unknown. Also, an easy equation to predict a_w values on food complex, like vegetables, meat, dairy products does not exist. The most important equations proposed from scientists show a good accuracy only in aqueous solutions. Moreover, the studies of dehydration mechanism are still poor to predict the behaviour of different raw materials during these treatments. So, the modulation of water availability is used from industries only in the case of dry food production.

2.3. The Effect of Water Activity on Food Safety and Quality

In 1970 Labuza presented a review concerning the effects of a_w on the most important degradation reactions of food. Figure 1 is a map of relative reaction rate as a function of a_w values [12]. More recently, several authors reviewed the effects of a_w on food quality [13,14,15,16,17].

From the map, in general, reaction rate increases with the increase of a_w .

At very low a_w values (0 – 0.2) water molecules are strictly bound to solid surface by ionic bonds, resulting unavailable to act as reactant or as good reaction medium: this is because a very high viscosity exists. This section of map stops with Brunauer-Emmet-Teller (BET) monolayer that for the majority of food is ranged between 0.2 and 0.3. Above this value, water exists as multilayer and its availability increases raising a_w values. As a result,

many reactions exponentially increase in particular in the range between 0.8 and 1 a_w values, in which water is only structurally entrapped in food, but not chemically bound.

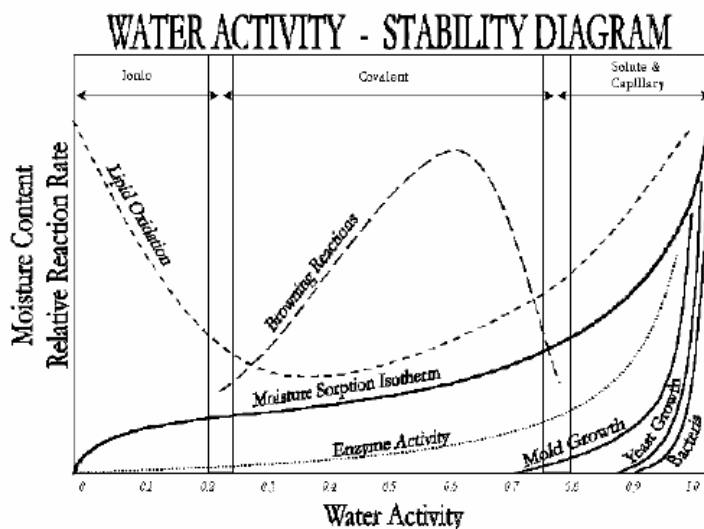


Figure 1. Stability map of food as a function of water activity [from 12].

Of course, for the practical importance on food safety, the effects of a_w on microbial growth were extensively studied in food area [18,19]. It is well known that when bacterial cells are exposed to osmotically hostile environment, they lose water and their natural turgor reduces. This phenomenon, named plasmolysis, proceeds until the cell cannot reproduce [20]. Experimentally, two different inhibition effects on growth curve could be observed: i) an increment of the lag phase; b) a reduction of the growth rate. These two effects are schematically represented in figure 2.

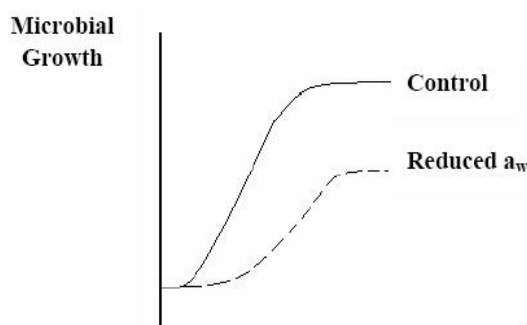


Figure 2. Schematic representation of the effects of a_w on microbial growth. [adapted from 18]

For instance, the lag time of *Staphylococcus aureus* is 1hr at 0.99 a_w value, 3hrs 30' at 0.94 and 13hrs at 0.90, when the a_w reduction was obtained adding sodium chloride to the solution. Several characteristics can affect the capability of microorganisms to grow in osmotically stressed media. The ability of microorganisms to regain natural turgor is directly

correlated with the possibility to concentrate compatible solutes inside cell membrane and then to solve the osmotic stress. This ability, named osmoregulatory mechanism, was widely studied by several authors [18,19,21,22,23].

Some humectants can exhibit a greater ability to inhibit microbial growth than others: this phenomena is called “solute effect” [18]. For instance, Gould and Measures [24] showed that *Clostridium botulinum* was inhibited in sodium chloride solution at 0.945 a_w value, but at 0.935 when glycerol was used as humectant. Besides, *Escherichia coli* needs a_w value of 0.95 and 0.935 in NaCl and glycerol solutions, respectively. Moreover the interaction with other factors like pH, oxygen, temperature, preservatives, radiation can affect the a_w threshold suitable to reduce microbial growth [18].

With almost no expectation, enzyme activity increases with increasing a_w value, due to the high level of system mobility, but some enzymes, such as lipase and lipoxygenase, show a high activity at very low a_w values (0.025 – 0.05) [25,26]. In this case water is not necessary to provide mobility of chemical species, because oil furnishes it, by plasticizing the system. For instance, Drapon [25] showed that a_w thresholds for olive oil and sunflower seed oil lipase were 0.025 and 0.05 respectively [27].

From the Figure 1 it is possible to notice an uncommon behaviour for lipid oxidation and browning reaction rate (Maillard reaction). In particular Maillard reaction shows a bell-shaped trend as a function of a_w . It is commonly accepted [28,29,30,31,32] that the first part of bell trend can be explained by a reduction of food viscosity that increases the mobility of reactant species, their probability to react and then the reaction rate. Also, when a_w value raises, the solubilization effect of chemical compound from the solid surface of food increases their concentration in the food system.

With the increase of a_w values, reaction rate reaches a maximum value, generally at 0.4–0.7 a_w , after that it decreases, because the “dilution effect” becomes predominant compared to “viscosity effect”; in this way, both the concentration of reactant species and the probability to react progressively reduce. Figure 3 shows the importance of the viscosity and dilution effects on Maillard reaction.

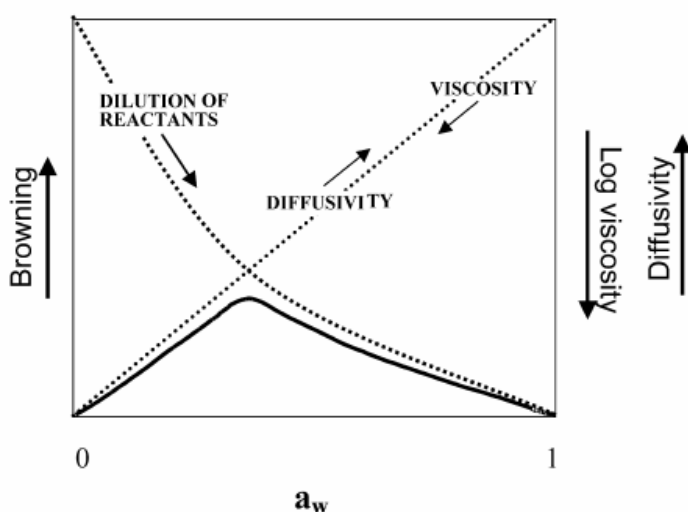


Figure 3. Viscosity and dilution effects on Maillard reaction as a function of a_w [from 32].

The trend of lipid oxidation as a function of a_w was extensively studied by Labuza [33] and Karel [34]. The authors proposed that water may exhibit both antioxidant and pro-oxidant effects. The former effect is shown at low a_w by: i) hydration effect of metal catalysts; ii) hydrogen bonding of hydroperoxides; iii) hindering the contact between oxygen molecules and solid surface; iv) promoting free-radical recombination. Instead, the pro-oxidant effects can be summarised as follows: i) increment of reactant mobility; ii) solubilization of reactant species; iii) matrix swelling that exposes new catalytic surfaces.

Karel [34] stated that water can affect lipid oxidation by influencing the concentration of radicals, the degree of contact and mobility of reactant, the relative importance of radical transfer versus recombination reactions.

Regarding the effects of water activity on food quality such as pigment and vitamin stability, protein denaturation, starch retrodegradation, textural properties, several papers are available.

In general, consumers cannot directly evaluate microbial quality, nutritional value and presence of anti-nutritional compounds; in the same way, they often cannot evaluate the aroma compounds and organoleptic quality like taste and texture. So, consumers can only evaluate the visual aspects to give a positive or negative judge and, among these the most important is colour.

Carotenoids are chemical compounds that confer red colour at vegetables and they exist in the stable *trans*-configuration. Heat treatment, acidification, light and oxygen can affect the stability of carotenoids; in particular the change from *trans* to *cis*-configuration produces colour modification in food [35]. Martinez and Labuza [36] stated that water is able to produce a protective effect on carotenoid isomerization; the authors showed that the colour stability of freeze-dried salmons was directly correlated with water activity. Following the authors, carotenoid denaturation could occur with similar mechanisms of lipid degradation (i.e. oxidation); then water could protect hydroperoxides from oxygen with the formation of insoluble metal hydroxides, that could not participate to the reaction.

Similar results were shown by Ramakrishnan and Francis [37] that showed protective effect of water on β -caroten, Apo-8'-carotenal and canthaxanthin (table 1). The greatest protective effect by water activity against color loss was at 75% of relative humidity; in fact, half-life values were 17.3, 21.6 and 49.5 days for β -carotene, Apo-8'-carotenal and canthaxanthin, respectively.

Table 1. First-order decoloration constant and half-life values for three carotenoids.

Relative Humidity (%)	β -Carotene		Apo-8'carotenal		Canthaxanthin	
	K	T _{1/2}	K	T _{1/2}	K	T _{1/2}
Dry	9.5	7.3	6.8	10.1	3.3	21.0
11	8.1	8.6	6.1	11.3	3.0	23.0
23	6.5	10.6	5.1	13.5	2.7	25.6
52	4.6	15.1	3.9	17.7	1.9	36.4
75	4.0	17.3	4.0	21.6	1.4	49.5

Decoloration or autooxidant constant in $\text{day}^{-1} \times 10^{-2}$; T_{1/2} = half-life in days (from 37)

From a sensory point of view, also chlorophylls are considered very important compounds, because they confer green colour on many vegetables. Their degradation into pheophytine occurs in acid media as a result of substitution of Mg with hydrogen atom at the centre of molecule. Some researchers found that the chlorophyll degradation in dried spinach occurred when the humidity content was 18%, but not with 2.5% of moisture [38]. Later, the studies published by Lajollo and Marquez [39] confirmed that chlorophyll degradation rate was less at low a_w value. This behaviour was explained by the reduction of media viscosity and thus with a decrement of reactant mobility.

The correlation between a_w values and the textural properties of food is obvious and this aspect was well reviewed by Bourne [40]. Here we would like only remember that texture properties, as organoleptic index, increase directly with a_w but, at the same time, safety decreases progressively. In 1969 Rokland [41] proposed a list of textural characteristics as a function of a_w (figure 4).

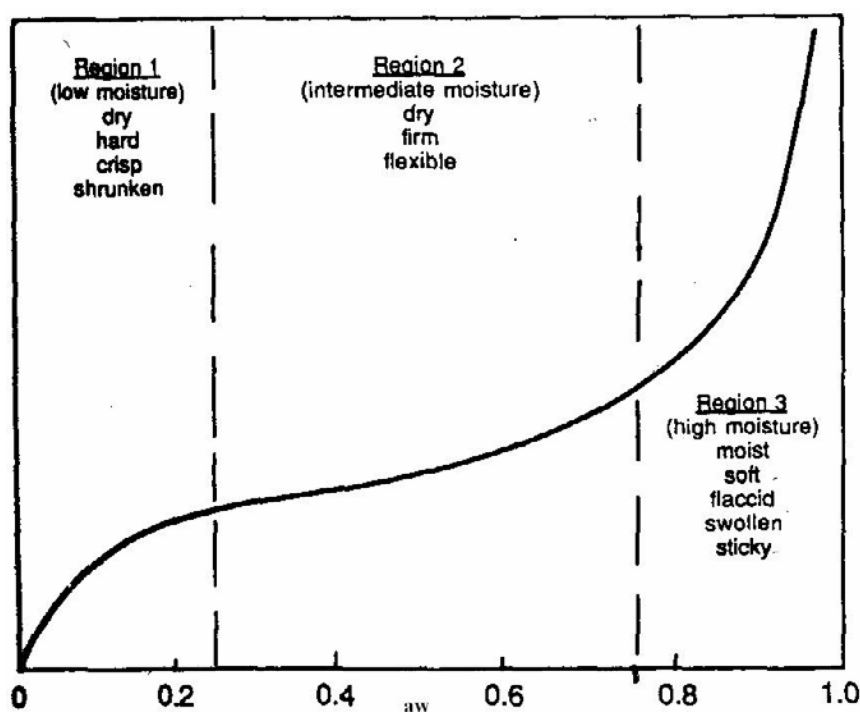


Figure 4. Schematic representation of textures as a function of a_w .

For the first part of sorption isotherm, the author used the terms dry, hard and crisp; in the region ranged between 0.3 – 0.7, food were named as dry, firm and flexible and in the last part of isotherm, the terms moist, soft and swollen were used.

3. Stabilization of Vegetable Creams by Water Activity Reduction: Case Studies

In general, the microbial stabilization of vegetables, for food with a long shelf-life as canned food, need the application of two essential treatments: i) pH reduction and ii) heating (pasteurization or sterilization). The first one is a pre-stabilization treatment that allows the application of a not too strong heating as pasteurization. In fact, when the greatest hazard is the toxin production by *Clostridium botulinum*, a pH value lower than 4.6 assures the inhibition of spore germination [42] and then the control of microbial load. However, the pH reduction often causes colour degradation and taste change; for instance *pesto*, as a typical Italian sauce, when is sold in glass pot as canned food, shows a brown colour due to chlorophyll degradation. For these reasons we studied the possibility to substitute the acidification process with a_w reduction by direct addition, in *pesto* sauce, of humectants until safety value for the sporulation of *Clostridium perfringens*, a microorganism that growth in similar conditions of *Cl.botulinum* [43]. Moreover, on the base of hurdle technology, we studied the possibility to apply a combined treatment of acidification-humectant addition, with the aim to obtain a pre-stabilization of pumpkin cream samples. In the next sections the principal results are reported.

3.1. Substitution of pH reduction with Humectant Addition as Pre-stabilization Treatment: a Study on Pesto Sauce

First, we performed some preliminary trials to evaluate the capability of different humectants (dry milk, KCl, NaCl, sucrose, fructose, lactose, threulose, glucose, potato starch, etc.) to reduce a_w on *pesto* sauce. Results showed that sodium chloride, potassium chloride, fructose and sucrose were the compounds that exhibited the highest capacity to bond water. Figures 5 and 6 show the trend of a_w values as a function of KCl-sucrose and KCl-fructose concentrations.

It is possible to observe that when fructose was added with KCl (figure 6), a higher reduction of a_w value was obtained compare to KCl-sucrose (figure 5). In fact, slope values of linear equation relative to the couple KCl-fructose were always greater than those relative to KCl-sucrose. Moreover, we observed the same trends when NaCl replaced KCl in aqueous solution (data not shown).

These results are not in accordance with those reported from Chirife et al [44] that showed a higher capability of sucrose to reduce water activity rather than fructose in aqueous solutions. This discordance can be explained taking into account two different aspects: a) the possible interaction of humectants with chemical compounds into a real complex food as *pesto* sauce; b) the use of percentage concentration (w/w) of humectants rather than their molar concentrations. In fact, when a constant percentage of sucrose and fructose were added into the samples, their differences in terms of molecular weight caused a great mole content of fructose into the *pesto* sauce samples.

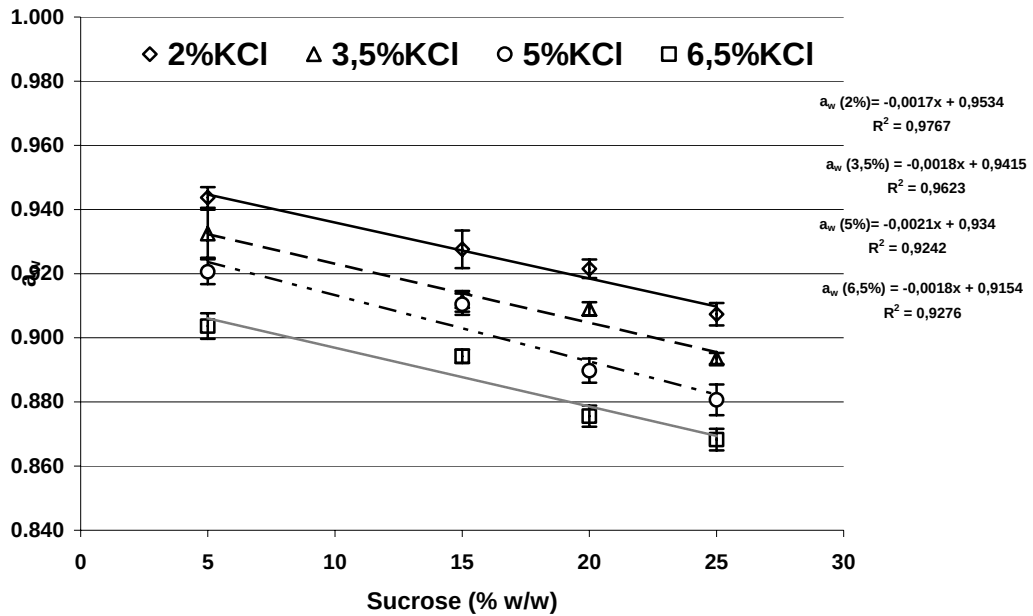


Figure 5 a_w values of *pesto* sauce as a function of KCl and sucrose concentration.

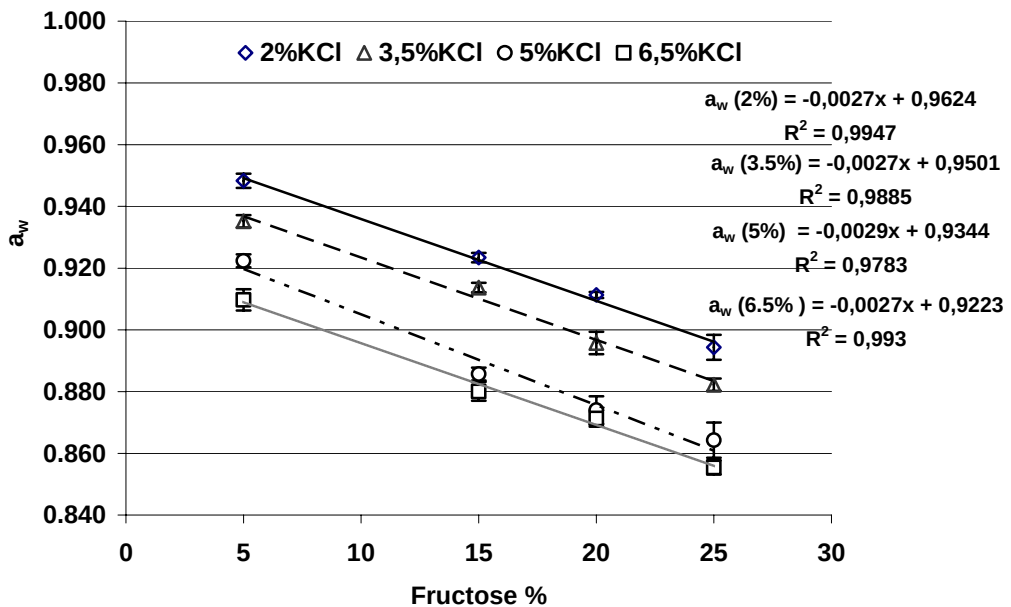


Figure 6. a_w values of *pesto* sauce as a function of fructose and KCl concentrations.

Starting from these preliminary results, we applied the Central Composite Design (CCD) methodology to evaluate the effects of two independent variables (a_w and storage

temperature) on dependent variables (microbial load, colour and pH) in *pesto* sauce samples. CCD's theory allows to obtain the suitable number of experiments by following equation [45]:

$$N_t = n_c + n^* + n_0 = 4 + 4 + 3 = 11$$

Where N_t , n_c , n^* and n_0 are the number of experiments, cube points, star points and central points, respectively. In table 2 is reported the Central Composite Design that we used for experiments.

Table 2. Central Composite Design

	Variables	
	a_w	Storage Temperature (°C)
+1,414	0,956	37,07
+1	0,95	35
0	0,935	30
-1	0,92	25
-1,414	0,914	22,92

In order to reach the a_w values shown in table 2, the equations obtained from the linearization of a_w values as a function of humectants concentrations were used (see equations reported in figures 5 and 6). All samples were prepared on the base of an industrial product and stored for 28 days. Sample were prepared by using both couple of humectants KCl-sucrose (CCD1) and KCl-Fructose (CCD2) thus obtaining two central composite designs.

Chemical, physical and microbial analyses were performed at time 0 and 3, 8, 15 and 28 days of storage.

In table 3 are reported the best fit equations relative to the effects of a_w on total count, cell and spore concentrations after 8 and 28 days for CCD₁ (KCl-sucrose) and CCD₂ (KCl-fructose).

Water activity always showed a significant effect on *Cl.perfringens* growth and, after 8 days of storage, total count and spore concentration were also affected by temperature for both CCDs. Moreover, in all cases, independent variables were directly correlated with independent ones, therefore the minimum value of microbial load was shown at minimum value of a_w and temperature.

To better understand the effects of a_w and temperature, figure 7 shows the iso-response surface relative to the total count after 8 days of storage for CCD₁.

Table 3. Results relative to the effects of a_w and temperature and their interaction on total microbial load (expressed as LogNt/LogN₀), cell concentration (expressed as Log UFC/g) and spores (LogNt/LogN₀) of *Clostridium perfringens*.

Time (days)	Dependent variables	Equations	F ^a	R ^b	SE ^c
CCD₁					
8	Total count	$1.002 * a_w + 0.0089 * T$	6615.8	0.999	0.033
	Cells	$4.285 * a_w$	1700.8	0.997	0.290
	Spores	$0.988 * a_w + 0.0079 * T$	6615.8	0.999	0.033
28	Total count	$1.314 * a_w$	29825	0.999	0.024
	Cells	$4.549 * a_w$	3518.3	0.998	0.222
	Spores	$1.267 * a_w$	12587	0.999	0.035
CCD₂					
8	Total count	$0.980 * a_w + 0.0078 * T$	5605.2	0.999	0.036
	Cells	$4.167 * a_w$	2586.3	0.998	0.238
	Spores	$0.894 * a_w + 0.0093 * T$	4834.00	0.999	0.038
28	Total count	$1.415 * a_w^2$	7845.2	0.999	0.046
	Cells	$4.783 * a_w^2$	2214.9	0.999	0.295
	Spores	$1.236 * a_w$	3672.1	0.999	0.063

^a value of Fisher's test

^b regression coefficient

^c standard error

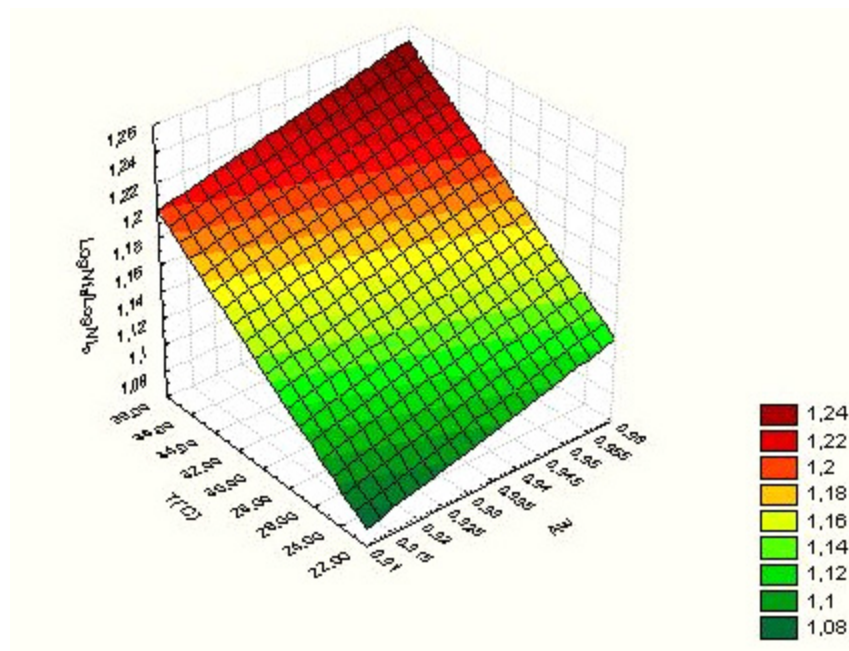


Figure 7. Iso-response surface relative to total count of *Cl.perfringens* as a function of temperature and water activity of *pesto* sauce samples after 8 days of storage.

From results, the different combinations of temperature and a_w allowed to reduce total count from 1.24 to 1.08. The same trend was also observed for spore (from 1.3 to 1.14) and cell (from 4.1 to 3.9) concentration (data not shown). Table 4 shows the Gompertz parameters and stability time for vegetative cells in CCD₁.

In particular, stability time (t.a.), is an useful parameter for the assessment of the stability of minimally processed food [46,47]; it is a threshold time after which the irreversible decay of quality occurs. Our results showed that t.a. was directly correlated with a_w and temperature values and reached a maximum value for sample prepared at 0.92 and stored at 25°C (run 1). It is also important to notice that our samples never reached the cell concentration threshold of 10^5 cell/g which can cause food poisoning [48].

Concerning the sensory quality of *pesto* sauce, figure 8 shows the Hue-Angle and chroma parameters of following samples: a) control (*pesto* prepared by fresh basil without humectant addition); b) reduced a_w sample (prepared by fresh basil at $a_w = 0.935$); c) CCD's samples and d) frozen semi-processed sample (after thawing).

Table 4. Gompertz parameters of vegetative form of *Cl.perfringens* in *pesto* sauce samples in Central Composite Design 1.

Run	a_w	T	A ^a	μ_{max}	λ	t.a. ^b
			CCD ₁			
1	0.92	25	3.719	3.529	0.160	6.666
2	0.92	35	3.880	2.415	0.158	4.270
3	0.95	25	4.415	2.481	0.159	4.895
4	0.95	35	4.320	2.163	0.157	4.078
5	0.914	30	3.802	2.079	0.171	3.564
6	0.956	30	3.926	1.387	0.153	2.246
7	0.935	22.93	3.826	1.775	0.181	2.999
8	0.935	37.07	3.772	1.755	0.277	3.214
9	0.935	30	3.784	2.135	0.181	3.711
10	0.935	30	3.780	2.025	0.161	3.397
11	0.935	30	4.050	2.170	0.165	3.919

^aGompertz parameters: A, maximum cell load attained at the stationary phase (Log CFU/g);

μ_{max} , maximal growth rate ($\Delta \text{Log[CFU/g]}/\text{day}$); λ , lag phase (days).

^bStability time (days).

Control and reduced a_w samples showed a typical green color with a Hue Angle value near to 118°; instead CCD₁'s samples and frozen semi-processed sample showed Hue angle values near to yellow region (98°). The color degradation of CCD's samples was caused by the thermal degradation of chlorophyll; in fact these products were submitted to pasteurization treatment.

The effect of heating on chlorophyll degradation is well known; for instance, van Loey et al. [49] showed that an increase of temperature (from 80 to 120°C) increased degradation rate of both chlorophylls *a* and *b* in aqueous extract of broccoli. Moreover, several scientists reported a very low thermal stability for chlorophyll *a* that is recognized as the most important pigment for green vegetables [50,51].

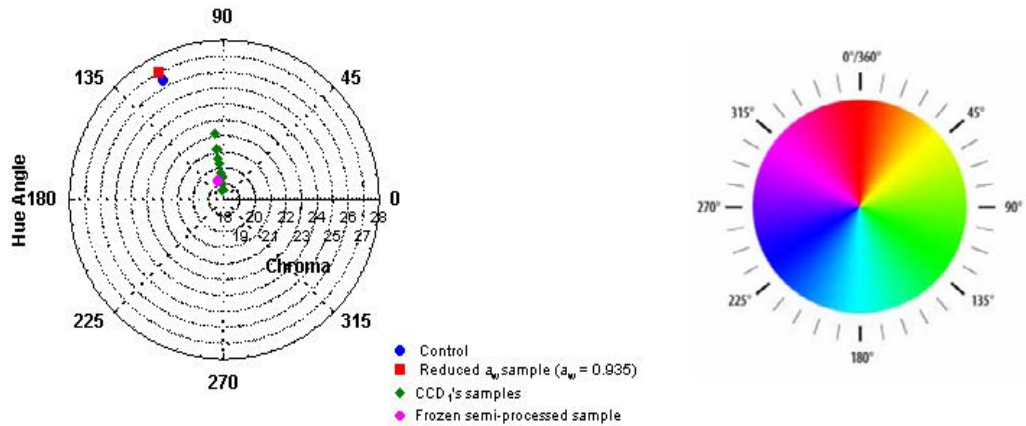


Figure 8. Hue angle and Chroma values of *pesto* sauce samples.

The same colour degradation was observed in our experiments when the raw material was an industrial frozen semi-processed product. In fact, the color parameter values of this semi-processed *pesto* sauce showed, also without humectants addition or heat treatment, a brown color compared to fresh basil. Samples prepared starting from fresh basil by adding humectants until to 0.935 a_w value (the central point of CCD) kept a green color close to fresh basil; in fact, it is possible to observe that hue angle and chroma values were overlapped (figure 8).

Moreover, in term of safety, the *pesto* sauce sample prepared from fresh basil and with a_w of 0.935 were stable, against the *Cl.perfringens* growth, for 28 days of storage without pasteurization treatment.

3.2. Acidification- a_w Reduction Combined Treatment: a Study on Pumpkin Creams

Often, the reduction of a_w , until values considered safe for the most dangerous microorganisms, need the addition of high concentration of humectants. These compounds are defined as “material that lower water activity but also allow products to retain their moist properties and give a plastic texture” [52]. A lot of chemical compounds show humectant properties: pentose, hexose, mannose, honey, invert sugar, glucose syrup, maldodextrins, cellulose, starch, alcohols and polyols, ethanol, sorbitol, glycerol, xylitol, polyethylene glycols, NaCl, KCl, $CaCl_2$, polyphosphates, milk serum, organic acids, proteins and their derivatives, etc. All these compounds, when used in food production, show different capability to reduce a_w , different plasticizing effects, antimicrobial actions, sweetening and confer on product different rehydration ability. Up till now, for canned food industry and in particular for fruit and vegetable cream products, very few humectants are normally used to reduce a_w and, among these, sugars and salts are the most applied. This is because many of above listed humectants produce strong change of viscosity, texture and taste. Moreover, also for sugars and salts, the concentration of humectants suitable to reach a_w thresholds for the

food safety often produce a modification on vegetable taste; in this way final products could be not accepted from the consumers.

So, on the base of the hurdle technology [53] we studied the possibility to apply a combined pre-stabilization treatment through a simultaneous a_w and pH reduction. In particular we here present the results concerning the direct addition of salt, sugar and lactic acid on pumpkin cream.

For these trials a Central Composite Design was applied with three independent variables (salt, sugar and lactic acid) and five levels (concentration of compounds) to evaluate the linear, quadratic and interactive effects of independent variables on a_w and pH values.

The results of statistical analysis are shown in table 5. For pH, all independent variables were evaluated as significant and we obtained three different partial equations useful to predict pH values as a function of independent variables. Instead, for a_w values only sucrose and NaCl were evaluated statistically significant as shown from the equation (table 5).

Table 5. Partial equations relative to the effects of independent variables on pH and a_w values.

Partial Eqn 1 Sucrose – Lactic acid
$pH = 5.5480 - 0.0106 * \text{Sucrose\%} - 7.5135 * \text{Lactic acid\%} + 10.34 * \text{Lactic acid\%}^2$
Partial Eqn. 2 NaCl – Lactic acid
$pH = 5.4895 - 0.0308 * \text{NaCl\%} - 7.5135 * \text{Lactic acid\%} + 10.34 * \text{Lactic acid\%}^2$
Partial Eqn. 3 NaCl – Sucrose
$pH = 4.6847 - 0.0308 * \text{NaCl\%} - 0.0106 * \text{Sucrose\%}$
$a_w = 0.9192 + 0.0310 * \text{NaCl\%} - 0.0018 * \text{Sucrose\%} - 0.0039 * \text{NaCl\%}^2$

Partial equations show that lactic acid affected pH by linear and quadratic terms while sucrose and NaCl only by linear correlation. As we expected lactic acid showed the maximum capacity to reduce pH in fact slope values (-7.5135 and 10.34 for linear and quadratic terms, respectively) was, in absolute value, greater than -0.0106 and -0.0308, slope values estimated for sucrose and NaCl respectively. Figures 9 and 10 show the trend of pH values as a function of sucrose-lactic acid and NaCl-lactic acid respectively.

According to partial equation, lactic acid was able to reduce pH value of 1 unit when its concentration increased from 0.04 to 0.32% (figures 9 and 10). With intermediate values of lactic acid and NaCl, a pH value less than 4.6, the FDA defined threshold to assure safety for low-acid food (2002), could be reached; for instance, using an acid concentration ranged between 0.14 and 0.16, a range of pH values just less than 4.6 could be obtained for any used NaCl percentages (yellow band in figures 10). Also, sucrose showed the capability to reduce pH of 0.2 unit (from 4.2 to 4.0) when its concentration increased from the minimum to the maximum value (figure 9). This effect was greater than salt effect which was able to reduce pH value only of 0.1 unit. Regarding the sucrose effect, we supposed that it could be caused by a decrease of water acting as solvent, as a result of bonds between water and sucrose. It is well known that sucrose is able to interact with water forming a cluster by hydrogen bonds: a reduction of water amount that acts as solvent could increase the ion hydrogen concentration and, as a consequence, modify the pH value.

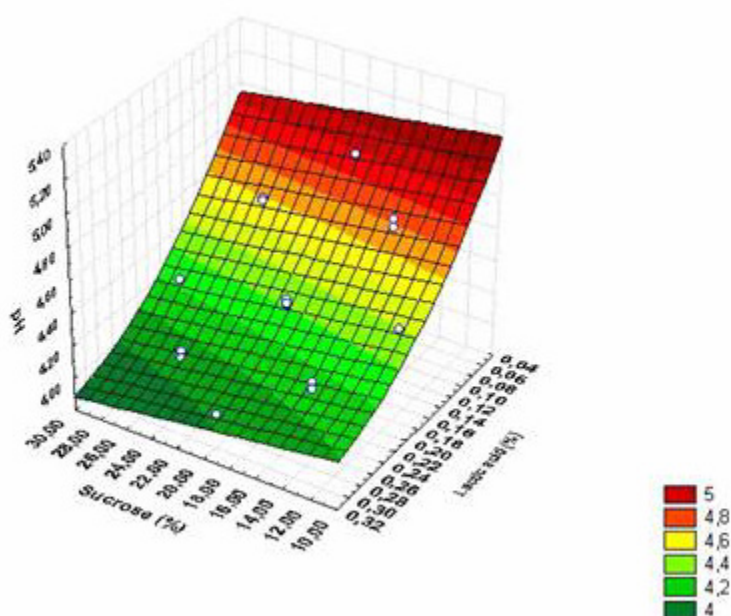


Figure 9. Iso-response surface relative to pH values as a function of sucrose and lactic acid concentration of pumpkin cream samples.

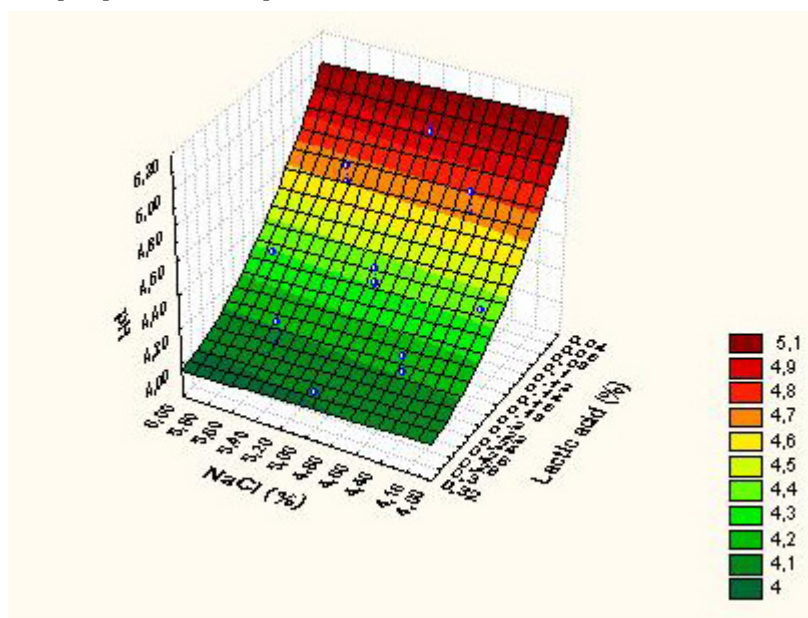


Figure 10. Iso-response surface relative to pH values as a function of NaCl and lactic acid concentration of pumpkin cream samples.

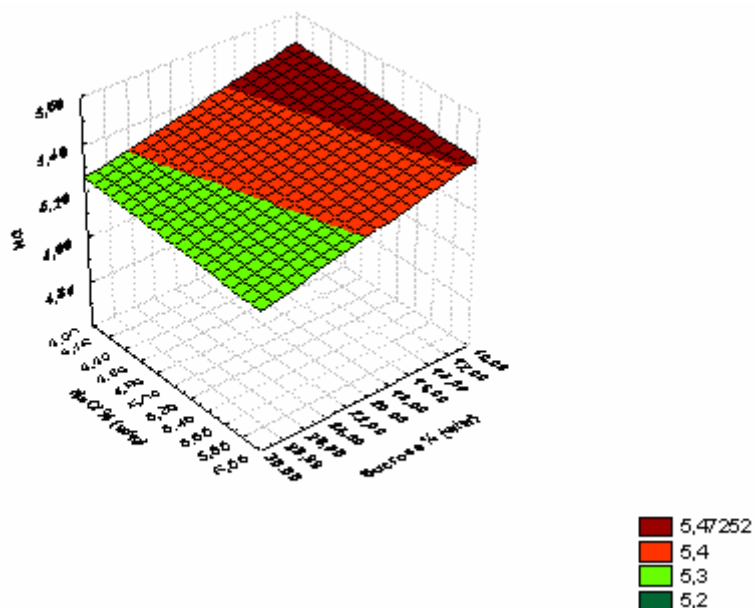


Figure 11. Iso-response surface relative to the pH values as a function of NaCl and sucrose concentration of pumpkin cream samples.

On the contrary, as known, the effect of salt is caused by its capability to affect the ionic strength of solution and consequently the constant of dissociation of organic acid [54]. Also, to better show the effect of sucrose on pH values, the iso-response surface of pH values as a function of sucrose and salt concentration is shown in figure 11.

As shown, pH values reduced from 5.4 to 5.2 when sucrose concentration increased from 10 to 30%.

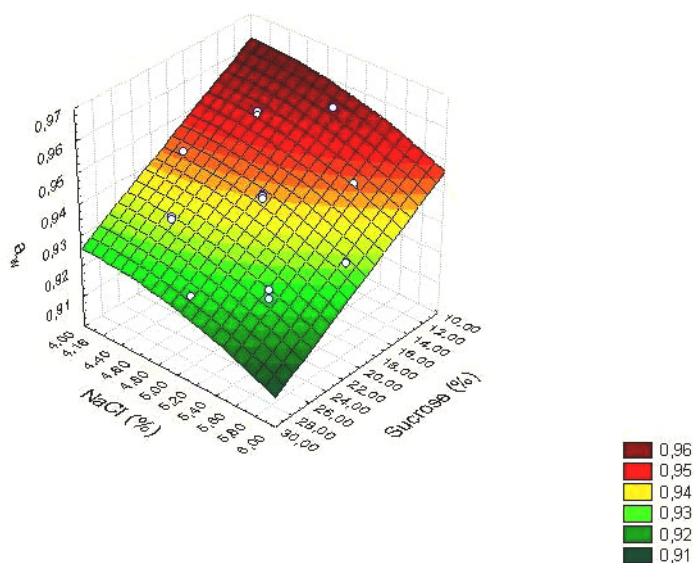


Figure 12. Iso-response surface relative to a_w values as a function of sucrose and NaCl concentration in pumpkin cream samples.

Regarding to the effects of independent variables on a_w , figure 12 shows the trend of water activity as a function of sucrose and sodium chloride concentrations.

Sucrose exhibited a greater capability to reduce a_w values compared to NaCl. The equation of table 5 shows significant effects of linear and quadratic terms for salt and only by linear term for sucrose. In particular, slope values for linear and quadratic terms of NaCl were 0.031 and -0.0039, respectively. Instead, sucrose linear term showed a slope value of -0.0018; so, we expected a greater effect of NaCl on the reduction of a_w value.

These slope values seem to be not in agreement with the trend of iso-response surface; nevertheless we should take into account that the concentration of sucrose was ranged between 10 and 30%, while the concentration of NaCl from 4 and 6%.

If slope values represent the effect of independent variables on dependent one, their values would be comparable only if the same concentration range were used.

4. Statistical Approach and Mathematical Model to Predict Water Activity in Complex Food

4.1. Theoretical and Empirical Model to Predict Water Activity: Advantages and Problems

The importance of water activity on safety and quality of food has been proved by an exhaustive scientific literature (see par 2.3). In the last 40 years, industries have increased the interest concerning this parameter with the aim to produce long shelf-life food and, if possible, to forecast a_w values in complex food. A very extensive bibliography concerning these aspects exists and it is very arduous to give an order at all empirical, mechanistic, thermodynamic and chemical equations that were proposed. Teng and Seow [55] stated: *“the goodness of a mathematical model to predict a_w values of complex mixtures need follow characteristics: i) must be based on theoretical principals; ii) must be easy to use; iii) must exhibit a good accuracy to predict intermediate moisture food (IMF)”*.

Raoult's law was the first equation proposed to predict water activity. This mathematical model is based on the correlation between a_w , vapour pressure and molar fraction of solution as follows:

$$a_w = \frac{P}{P_0} = \chi_w = \frac{\eta_w}{\eta_w + \eta_s} \quad (8)$$

where χ_w is the water molar fraction, η_w and η_s are the mole numbers of water and solutes into the solution respectively. This equation is not very accurate due to the assumption of ideal behaviour of solution. Later, an error factor for non-ideal solution was introduced into the equations:

$$a_w = \gamma_w \times \chi_w \quad (9)$$

where γ_w is the activity coefficient.

Starting from thermodynamical consideration, Norrish [56] proposed an equation to predict a_w of non-ideal aqueous solutions:

$$a_w = \chi_w \times \exp(K \times \chi_s^2) \quad (10)$$

where χ_w and χ_s are the molar fraction of water and solutes respectively and K is a constant of equation. It is easy to obtain the K values, carefully measuring the slope of curves obtained reporting $\ln(a_w)$ as a function of $K \times \chi_s^2$. Several values of K are reported in literature for different solutes [57,58]

For a multi-component solutions the Norrish's equation is mathematically more difficult:

$$\ln(a_w) = \ln(\chi_w) + \left[\left(K_1^{1/2} \right) \times \chi_1^2 + \left(K_2^{1/2} \right) \times \chi_2^2 + \dots \dots \dots \left(K_i^{1/2} \right) \times \chi_i^2 \right] \quad (11)$$

This equation was validate by Vega-Mercado and Barbosa-Canovas [59] which predicted on a_w value of 0.78 for a sucrose aqueous solution (2.44/1 w/w) despite an experimental value of 0.74.

Maybe, the most popular model used to predict a_w of solutions is the Ross's equation. Based on thermodynamic and starting from Gibbs Dhuem:

$$\sum_i n_i d(\ln a_i) = 0 \quad (12)$$

where n_i is the number of moles of component i and a_i is the activity of component i. For binary solutions (water and solute) eq. 12 can be expressed as follows:

$$55.5 d(\ln a_w) = -m_a d(\ln a_w) \quad (13)$$

since, by the definition of molality, 1 kg of water (55.5 moles) contains m_a moles of solutes. Starting from eq. 13 and by appropriate integration it is possible to obtain following model for multicomponent solution Ross [60]:

$$\ln(a_w) = \ln(a_{w1}^0) + \ln(a_{w2}^0) + \ln(a_{w3}^0) + \dots \dots \dots + \ln(a_{wi}^0) \quad (14)$$

or also,

$$a_w = a_{w1} \times a_{w2} \times a_{w3} \times \dots \dots \times a_{wn} = \prod a_i^0 \quad (15)$$

Ross stated that water activity values of a multi-component solutions is the product of a_w values of binary solutions obtained from each solute inside the complex mixture. Several authors used this equation to predict the a_w values of sugars, salts and organic acid solutions obtaining a good accuracy [61,62,63]. Also, Herman et al. [64] used Ross's equation to

predict the isotherm of pineapple's samples. Moreover, they did notice that an increase of temperature increased the difference between experimental and predict a_w values.

Practically, the main problem related to the use of this equation, from industrial point of view, is the necessity to know the a_w^0 values for each component of food complex. Some values for different compounds are reported in bibliography, but, if is not the case, some authors proposed the use of new equations to calculate the a_w^0 values on the base of molality of components or electric charge value as in the case of electrolytic compounds [65,66]. For instance, Chen et al [67] proposed the following equation to predict the a_w^0 values of binary solutions:

$$a_w = \frac{1}{1 + 0.0018 \times (\beta_0 + B_m^n) \times m} \quad (16)$$

where m is the molality of solution and β_0 and B are constants.

Pitzer [68] proposed an equation to predict a_w values of electrolytic solutions as follows:

$$a_w = \exp(-0.01802\Phi \sum M_i) \quad (17)$$

where Φ is the osmotic coefficient and M is the molality of each ion of the solution [69].

Also, Lang and Steinberg [70] proposed a model to forecast the a_w value of multicomponent solutions.

$$\text{Log}(1 - a_w) = (MW - \sum (a_i w_i) / \sum (b_i w_i)) \quad (18)$$

where $MW = (m_i) \times (w_i)$, M is moisture of multicomponent solution, W is dry matter content, m_i and w_i are moisture and dry matter content of each component of solutions, respectively; a_i and b_i are constants of Smith's equation (intercept and slope values, respectively).

An important modification of Ross's equation was carried out from Lerici et al. [71]. They correlated a_w with a very easy parameter: the percentage of solutes into the solution:

$$a_w = m \times \left(\frac{S}{W} \right) + q \quad (19)$$

where S and W are the weights of solutes and water of solutions, respectively; m and q are the slope and the intercept values of the linear equation; it is to be underlined that m value physically means the capability of solute to bond water. Moreover this equation was introduced into the Ross's equation obtaining:

$$a_w = \left(m_1 \times \frac{S_1}{W} + q_1 \right) \times \left(m_2 \times \frac{S_2}{W} + q_2 \right) \times \left(m_3 \times \frac{S_3}{W} + q_3 \right) \times \dots \times \left(m_i \times \frac{S_i}{W} + q_i \right) \quad (20)$$

In this way the prediction of a_w value of multicomponent solution become possible by measuring the weight of each component into the complex solution.

Also, in table 6 others equations proposed to predict water activity values of food are reported.

Nevertheless, even if some of mathematical models above reported show a good accuracy in the prediction of a_w values, they could not be used in practical purposes. Strictly speaking, nowadays industries have not a useful tool to predict water activity. The greatest hurdle to their application is the necessity to well know some chemical or physical parameters and a good capacity to data handling; in fact, the proposed models are not mathematically easy. Moreover, a lot of these equations has been validate only on binary or multicomponent aqueous solutions, but very few papers concerning the prediction of a_w on complex food like biscuits, emulsions, sweets, vegetable creams, meat and diary products exist. In real complex food many interactions among chemical compounds (sugars, salt, ions, etc.) could occur and their behaviours could be often too far from the model systems.

So, for complex food an useful mathematical model to predict water activity should be:

- a) mathematically easy (or easy to use);
- b) directly correlated with parameters easy to measure (i.s. weight, percentage);
- c) sufficiently accurate;
- d) able to predict a_w in different binary solutions (sugars, ions, acids, etc);
- e) able to predict a_w in complex food;
- f) able to explain the interaction among different added humectants.

4.2. Study of empirical equation to predict a_w values in vegetable creams.

The possibility to obtain an empirical equation to predict a_w values on vegetable creams was studied. In particular a mathematical model with following characteristics was looked for: a) easy to use; b) directly correlated with the percentage of humectants used in vegetable creams; c) able to be used choosing the humectant concentrations connected to desired organoleptic characteristics.

First, five concentrations of potassium chloride and fructose were combined to obtain 25 aqueous solutions. In particular concentrations of potassium chloride and fructose ranged between 4 and 20% and from 5 to 25% were respectively were used. These concentrations were chosen based on preliminary trials, in order to obtain a_w values from 0.79 to 0.96. For each of these solutions a_w was measured (in triplicate) by hygrometer (Aqualab, Decagon Device). After, a non linear-regression analysis was carried out on experimental data with three different mathematical models:

Eqn 1: $y = B_0 + \sum B_i x_i + \sum B_{ij} x_i x_j$ – linear model;

Eqn 2: $y = B_0 + \sum B_i x_i + \sum B_{ii} x_i^2 + \sum B_{ij} x_i x_j$; non linear quadratic model ;

Eqn 3: $y = B_0 + \sum B_i x_i + \sum B_{ii} x_i^3 + \sum B_{ij} x_i x_j$ – non linear, cubic model;

Table 6. A resume of the equations proposed to predict water activity in food

1) $M = \delta^{1/n} K (a_w)^{1/n}$	McGavack – Patrick, 1920
2) $\ln (1/a_w) = K_2 K_1^M$	Bradley, 1936
3) $\frac{a_w}{(1-a_w) M} = \frac{1}{M_m C} + \frac{a_w (C-1)}{M_m C}$ (eq. BET)	Brunauer <i>et al.</i> , 1938
3 ^{bis}) $M = \frac{M_m C a_w}{(1-a_w)} * \frac{1-(n+1) a_w^n + n a_w^{n+1}}{1+(C-1) a_w - C a_w^{n+1}}$	Brunauer, 1945
4) $\ln A_w = B - A/M^2$	Harkins – Jura, 1944
5) $A + B a_w - C A_w^2 = a_w/M$	Hailwood – Horrobin, 1946
6) $M = a \left[\frac{a_w}{1-a_w} \right]^n$	Oswin, 1946
7) $M = M_b - M_a \ln(1-a_w)$	Smith, 1947
8) $a_w = \exp \left[-\frac{a}{RT} \left(\frac{M}{M_m} \right)^r \right]$	Halsey, 1948
9) $1 - a_w = \exp (-gTM^n)$	Henderson, 1952
10) $1 - a_w = \exp (-J_1 T_1^h M^{J_2 T_2 h})$	Day – Nelson, 1965
11) $\ln a_w = (-a/RT) \exp (-bM)$	Chung – Pfof, 1967
12) $M = (a/\ln A_w) + b$	Kuhn, 1967
13) $\ln \left(\frac{100 - \%H_2O}{\%H_2O} \right) = \ln A - r a_w$	Caurie, 1970
14) $a_w = \frac{a + M}{b + M}$	Mizrahi <i>et al.</i> , 1970
15) $\ln [M + \sqrt{(M^2 + M_{0.5})}] = b a_w + p$	Iglesias – Chirife, 1976

The goodness of fitting was evaluated by correlation coefficient (r), p-level and standard error (s.e.). The best fit equation obtained from statistical analysis was used to predict a_w values. The model was validate in aqueous solution, in mushroom aqueous extract and in vegetable creams.

The results of statistical analysis showed that the non linear quadratic equation was the best to explain the trend of experimental data. In fact, correlation coefficient values were 0.985, 0.996 and 0.994 respectively for linear, quadratic and cubic models. So, the following model was obtained and used for the experiments:

$$a_w = 0.955 + 0.00161 * \text{fructose} (\%) - 0.00019 * \text{KCl}^2 (\%) - 0.000067 * \text{fructose}^2 (\%) - 0.000151 * \text{KCl} (\%) * \text{fructose} (\%).$$

Results showed that interactive term was statistical significant and it showed an inverse correlation with a_w values. Figure 13 shows both the trend of experimental values (open

points) and the surface obtained by non linear quadratic model. According to equation, the figure shows that KCl reduced a_w values greater than fructose. In fact, going from maximum to minimum KCl concentration, a_w reduced from 0.96 to 0.87; instead, going from 5 to 25% of sucrose, a_w values decreased only of 0.2 unit (from 0.96 to 0.94). The variance explain values of 99.12 stated the high capacity of mathematical model to fit a_w values.

By the above equation it was possible to choose a desired a_w value and the concentration of one of the used humectants with the aim to obtain a product with the desired organoleptic features (i.e. salty or sweet). After, it was possible to calculate the concentration of the second humectant necessary to reach the a_w value preliminary chosen. In figure 14 the concentrations of fructose that it is possible to choose as a function of a_w values are shown.

$$a_w = 0.955 + 0.00161 * \text{Fructose\%} - 0.00019 * \text{KCl}^2\% - 0.000067 * \text{Fructose}^2\% - 0.000151 * \text{KCl\%} * \text{Fructose\%}.$$

Variance Explained = 99.12%

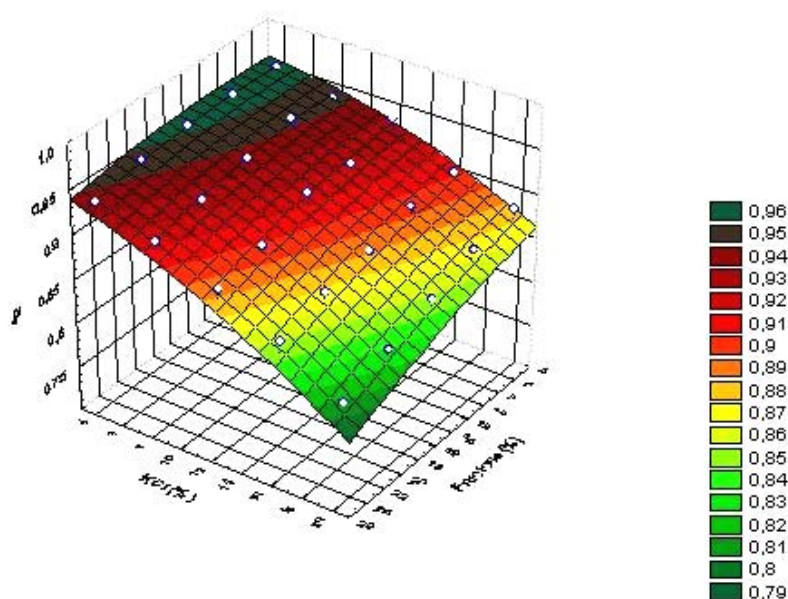


Figure 13. Surface plot relative to a_w values as a function of KCl and fructose concentration.

For instance, if we would like to obtain a a_w value of 0.90 it is possible to choose any concentration of fructose between 5 and 25% and then compute, by the proposed equation, the concentration of KCl necessary to reach the a_w value of 0.90. In the same way, different concentrations of KCl could be chosen as a function of a_w , with the aim to obtain a salty product (data not shown).

On the base of previous discussion, samples of aqueous solution, aqueous extract and mushroom cream were prepared (in triplicate) with 5 different concentrations of KCl and fructose. Four a_w values for aqueous solution and 5 values for aqueous extract and mushroom creams ranged between 0.82 and 0.95 were chosen to evaluate equation proposed. So, 75 samples were prepared and a_w were then measured. The correlation between experimental and predicted a_w values for aqueous solution is shown in figure 15.

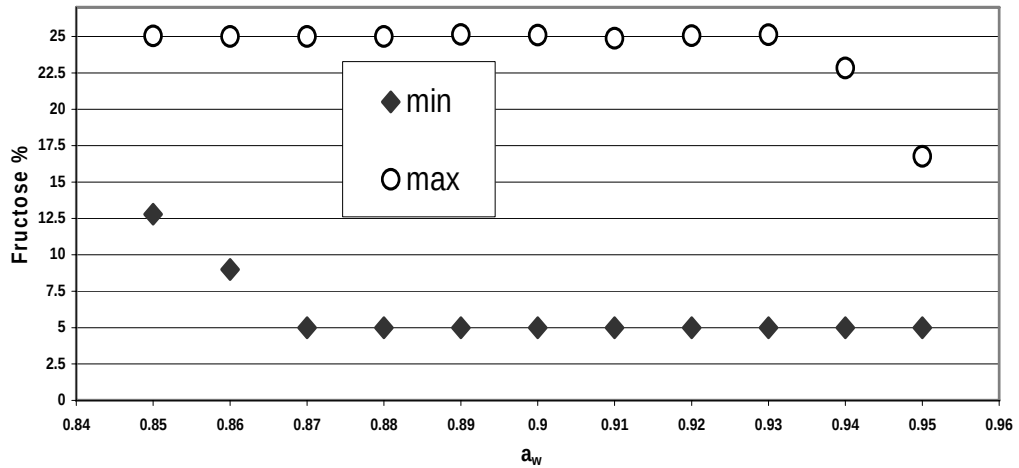


Figure 14. Range of fructose concentrations that is possible to choose in relation to desired a_w values and organoleptic characteristics.

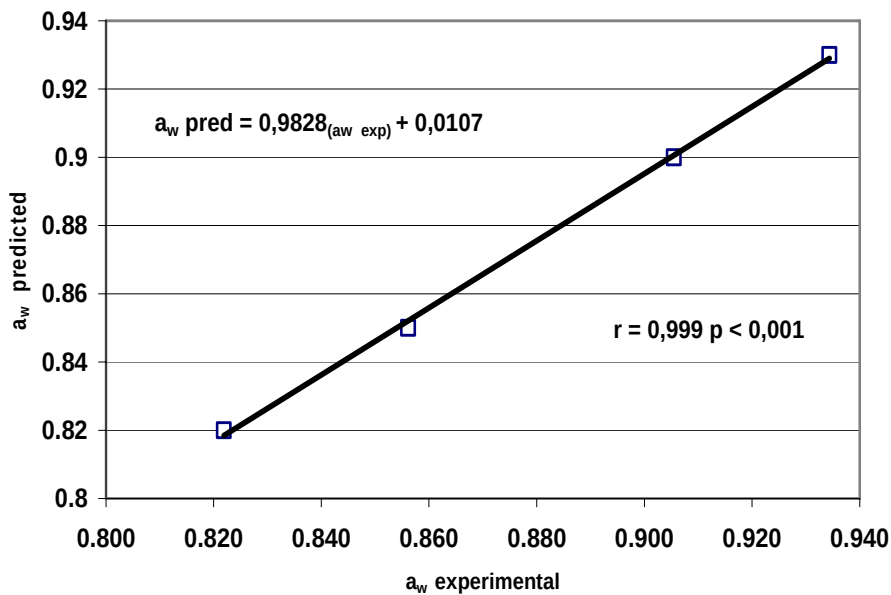


Figure 15. Experimental and predicted a_w values of aqueous solution prepared with KCl and fructose at different concentrations.

It is possible to observe a good correlation between predicted and experimental values. In particular, correlation coefficient of 0.999 and p-level lower than 0.001 prove the high capability of equation to predict a_w values. Moreover the intercept and slope of linear equation (0.0107 and 0.9828 respectively), stated the accuracy of a_w value prediction. In table 7 are shown the couples of KCl and fructose concentrations used to reach the chosen a_w value, the corresponding experimental a_w and statistical data: standard deviations (dev. st.),

variation coefficients (c.v.%) and percentage of prediction error (PE%), calculated as follows [72]:

$$PE\% = \left(\frac{a_w(pred) - a_w(exp)}{1 - a_w(exp)} \right) * 100$$

Table 7. Results relative to the prediction of a_w values on mushroom cream samples with addition of KCl and fructose.

Fructose %	KCl %	a_w predicted	a_{w1}	a_{w2}	a_{w3}	a_w experimental	dev. st	v. c. (%)	PE %
24,670	18,5	0,82	0,810	0,828	0,845	0,828	0,018	2,115	-4,449
23,947	18,8	0,82	0,831	0,832	0,827	0,830	0,002	0,301	-5,824
22,722	19,3	0,82	0,836	0,825	0,815	0,825	0,011	1,273	-3,053
21,217	19,9	0,82	0,826	0,824	0,827	0,826	0,002	0,185	-3,250
21,471	19,8	0,82	0,825	0,820	0,824	0,823	0,003	0,321	-1,695
						a_w average: 0,826			
24.26	12.4	0.88	0.876	0.870	0.875	0.874	0.003	0.368	5.013
21.3	13.6	0.88	0.871	0.874	0.874	0.873	0.002	0.198	5.512
8.13	18	0.88	0.873	0.867	0.869	0.870	0.003	0.351	7.928
15.89	15.6	0.88	0.878	0.867	0.865	0.870	0.007	0.805	7.692
5.8	18.6	0.88	0.890	0.865	0.870	0.875	0.013	1.512	4.000
						a_w average: 0.872			
23.458	10.2	0.9	0.892	0.894	0.889	0.892	0.003	0.283	7.332
19.398	11.8	0.9	0.890	0.895	0.894	0.893	0.003	0.297	6.169
16.036	13	0.9	0.889	0.890	0.893	0.891	0.002	0.234	8.186
9.490	15	0.9	0.894	0.894	0.890	0.893	0.002	0.259	6.832
18.312	12.2	0.9	0.896	0.900	0.900	0.899	0.002	0.257	1.316
						a_w average: 0.894			
23.502	5.6	0.93	0.922	0.929	0.928	0.926	0.004	0.410	5.569
19.437	7.2	0.93	0.923	0.924	0.925	0.924	0.001	0.109	8.460
14.666	8.8	0.93	0.924	0.920	0.924	0.923	0.002	0.250	9.483
10.239	10	0.93	0.915	0.920	0.917	0.917	0.003	0.274	15.323
6.355	10.8	0.93	0.925	0.920	0.921	0.922	0.003	0.287	10.256
						a_w average: 0.922			
11.13	5.4	0.95	0.955	0.958	0.953	0.955	0.003	0.263	-11.940
14.66	4.6	0.95	0.955	0.953	0.955	0.954	0.001	0.121	-9.489
8.521	5.8	0.95	0.958	0.955	0.958	0.957	0.002	0.181	-16.279
15.395	4.4	0.95	0.960	0.956	0.954	0.957	0.003	0.319	-15.385
13.047	5.0	0.95	0.955	0.955	0.957	0.956	0.001	0.121	-12.782
						a_w average: 0.956			

In particular, data reported in table 7 are referred to mushroom's cream samples. From results, the proposed equation seems to be able to predict, with high accuracy, the a_w values of mushroom cream; in fact, in all cases the maximum error percentage (PE) is equal to -16.279, which, in absolute terms, correspond to 0.007 units of a_w , comparable with accuracy of instruments or precision of standard solution normally used to calibrate hygrometers (± 0.003 unit, Decagon Devices, Inc. Pullman, USA). The difference between experimental and predicted a_w values of mushroom cream samples are graphically shown in figure 16.

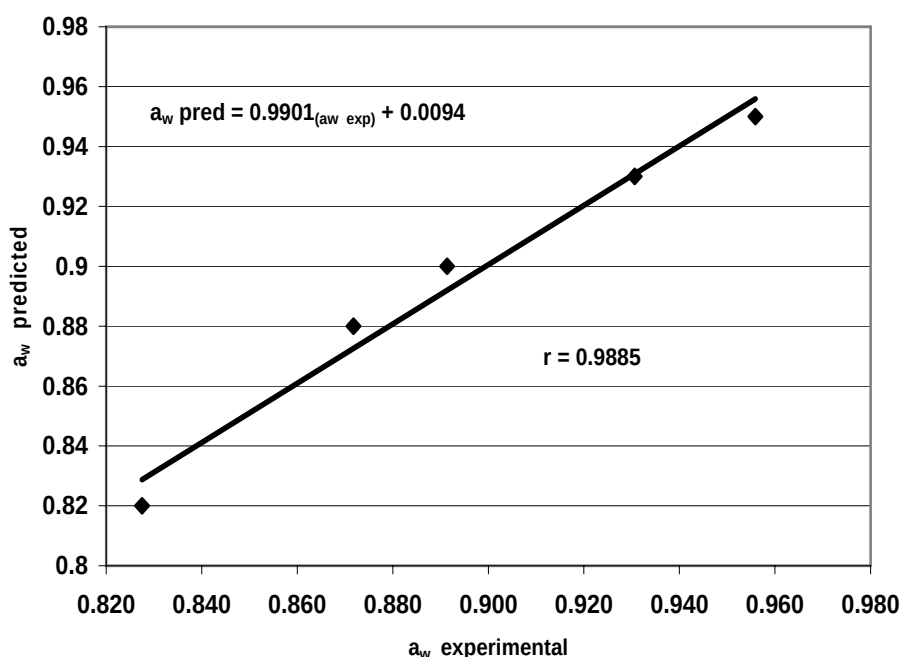


Figure 16. Experimental and predict a_w values of mushroom cream prepared with KCl and fructose at different concentrations.

Also in this case the correlation coefficient and the p-level stated a good correlation between experimental and predicted a_w values; moreover, the slope and intercept values equal to 0.991 and 0.0094 stated that experimental values are very close to the predicted ones.

With the aim to better validate the proposed equation, we verified it in a different type of raw material (apple cream) and also on mushroom cream added with different concentrations of olive oil (a typical ingredient used to prepare vegetable creams). Results obtained from apple cream showed a maximum PE% values of 12.0127 which, in absolute value, correspond to a pure error of 0.021 unit of a_w ; moreover, a correlation coefficient of 0.997 and p-level less than 0.001 of linear regression between experimental and predicted values stated that the accuracy of model did not change when the raw material changed. Moreover a very good correlation between predicted and measured data was observed also for mushroom cream added with olive oil (data not shown).

5. Water in Food in Terms of Dynamics

As previously discussed, nowadays the main parameter used to obtain information about the state of water in food is water activity. Nevertheless, in the last 10 years the interest about a_w decreased; in fact, several scientists showed that this parameter cannot explain some commonly observed behaviours of food.

Water activity is defined in terms of thermodynamic equilibrium of aqueous solutions by following equation [73]:

$$\mu_w = \mu_w^0 + RT \ln a_w$$

Nevertheless, it is correct only for ideal solutions. The aqueous solutions are defined as ideal if the molecules do not preferentially interact with others (or with solvent); moreover, for ideal solutions, any volume of element can be occupied with equal probability from solvent or solute molecules. In this condition above equation is true and water activity is equal to molar fraction of water (χ_w). Practically, this is an unusual condition for complex food during both industrial processes or storage time.

Felix Franks [74] showed that the effect of aggregation of solute molecules and the preferential interaction between solvent and solute molecules can modify water activity. Furthermore, different solutes affect a_w values in different ways. In fact, it is well known that sodium and potassium chloride aqueous solutions at the same concentration show different a_w values. This experimental evidence cannot be explained in terms of water activity in fact, colligative properties are related first with the concentrations of solute and then with the type of compounds by dissociation coefficients (i) that is the same for both NaCl and KCl.

Recalling the definition of water activity, of course if water diffuses slowly on surface of food, the equilibrium of vapour pressure will be reached after long time. Under this conditions (kinetic control) the a_w measured by the common instruments (hygrometer) is only the relative vapour pressure (RPV) and it cannot be directly correlated with a_w values. Some examples of food governed by dynamic rather than thermodynamic are the following: butter, ice cream, bread dough, mayonnaise, freeze-dried proteins, bloom on chocolate, gelatin desserts [73].

Moreover, the Labuza's stability map above reported (see par 2.3) shows the correlation between the rate of degradation reactions (kinetic parameter) and a_w values (thermodynamic parameter) and this cannot be recommended in practical purposes [73].

Besides, it is not clear how water activity acts at molecular level on microbial growth. In terms of water activity, microbial cells are usually, but not correctly, thought as osmometer. Van den Berg [75] cited several papers in which microbial showed the following behaviours: a) different microbial growth at identical a_w values prepared with different solutes; b) identical microbial growth at different a_w values prepared with different solutes. So, microorganisms differently respond to identical a_w values, set by different solutes; furthermore many food are not in equilibrium state, then, the use of a_w concept cannot guarantee the accurate prediction of food shelf-life [73]. The assumption of a well correlation between a_w and microbial growth for the production of new intermediate moisture food could increase the risks for human health.

For all these reasons in the least years the interest of scientists focused on the concept of “mobility water” rather than “state of water” increased progressively.

Slade and Levine [72] pointed out the key elements of this new approach based on dynamic, recognizing the importance of following aspects:

- the behaviour of food is governed by dynamics rather than thermodynamics;
- the importance of T_g temperature of food as parameter that can determine processability, properties, quality and safety of food;
- the central role of water as a ubiquitous plasticizer compound;
- the effect of water on T_g temperature and, as a consequence, the non-Arrhenius behaviour of food at $T > T_g$ (in the rubbery state);
- the importance of non-equilibrium glassy-solid and rubbery state in all real food products and processes.

These considerations recognize the glassy state as the kinetically stable state in which food degradation reactions and microbial growth cannot occur; despite, rubbery state is recognized as a kinetically unstable state.

Practically, food are in glassy state when are kept at $T < T_g$: in this condition, degradation reactions occur with so long time that it is not possible to observe them in real time (metastable state). Starting from these assumptions, the measure of glassy state temperature by thermal analysis (DSC) was emphasized as the parameter to evaluate the effects of availability of water on food quality. So, in the last 40 years several scientific papers concerning the effect of T_g on food degradations were published, but results were, often, contradictory. For instance, in figure 17 the rate of non-enzymatic browning, measured by O.D. (optical density) at 446 nm as a function of $T - T_g$ values, is shown [76]. The K value increases with the increase of $T - T_g$ until a maximum value close to 0, after which K decreases again. Only the first section of trend is in accordance with glassy state theory. The authors supposed that in rubbery state ($T - T_g > 0$) the collapse of matrix could produce a reduction of diffusion pathways for reactants and their reduce the possibility to react.

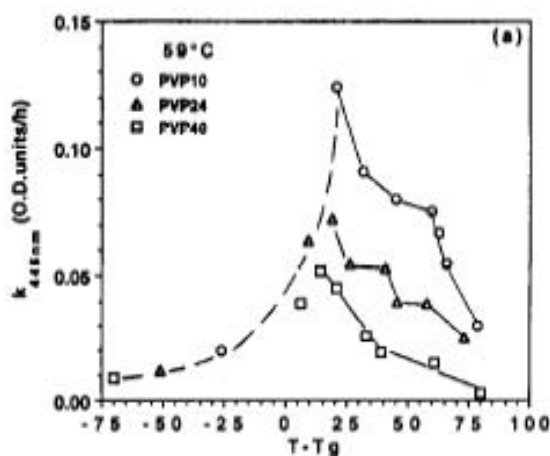


Figure 17. Zero-order rate constant vs. $T - T_g$ for xylose-lysine reaction in different matrix at 59°C. [76].

Moreover, as shown in figure 17, the rate of reaction is greater than zero in glassy state. This is not in accordance with theory that states operationally immobile, stable and unreactive the situation in glassy state [73].

Schebor et al [77] studied the effects of glassy state on thermal inactivation of invertase in different dried matrices. Following the authors: *“results suggest that the thermal enzyme inactivation in dried amorphous system cannot be predicted on the basis of glassy transition theory”*. Also, they wrote *“the definition of stability maps as proposed by Slade et al (1989) and Slade and Levine (1994) in which T_g s of major constituents provide a boundary between regions of low mobility (glasses) and increases mobility (rubbers) cannot be used as the sole important parameter for predicting the stabilization of invertase in amorphous dried system”*. Moreover, results obtained by Craig et al [78] showed that, although glassy state exhibits high viscosity and low mobility, there is a sufficient mobility of chemical compounds to react among them.

So, authors exposed two different considerations regarding to the non-zero rate constant of Maillard reaction in glassy state: a) if glassy state would be obtained by freeze-drying, the reactants could be so near that they can collide and react without moving [79] ; b) first part of reaction could occur inside the holes in model system obtained by freeze-drying process [80]. Probably, inside this holes, the reactants kept a sufficient mobility to react.

Based on previous discussion, in the last 10 years the interest concerning nuclear magnetic resonance (NMR) techniques, as the most important method to measure mobility water of food, has been increased progressively. An exhaustive bibliography on theory of this spectroscopy technique is presented in many books [81,82,83,84].

In this chapter we will discuss only about the use of NMR and MRI for water mobility measure. Nevertheless, is necessary recall some principles that govern the two main parameters measured by NMR: T1 and T2 also called *spin-lattice relaxation time* and *spin-spin relaxation time* respectively. In particular, the spin-lattice relaxation is the interaction between nuclear spin dipole and fluctuating magnetic fields, due to motion of the surrounding dipole in the lattice (defined as environment surrounding the nucleus). Instead, spin-spin relaxation is caused by three main sources: i) movement of the adjacent spins due to molecular vibration or rotation; ii) inhomogeneity of magnet; iii) sample-induced inhomogeneity.

The key point for our discussion is that if water is free (bulk water), it has high mobility and shows a long relaxation time or low relaxation rate ($R=1/T$); but if water is tied by hydrogen bonds or electrostatic (i.e. protein) it exhibits a low mobility and a short relaxation time or high relaxation rate. So, usually T1 and T2 are used to define the state of water in different food.

Leung et al. [85] used T1 and T2 to study the state of water in bread during staling. They showed that both T1 and T2 decreased during storage time of bread, indicating a reduction of mobility water in spite of constant moisture. Leung et al. [86], using CPMG pulse sequence, found two fractions of water in flour dough with two different degrees of freedom; the first with T2 about 54 ms and the second with T2 of 12 ms.

Vittadini et al. [87], studied mobility of water in cellulose, comparing data obtained by ^1H and ^2H NMR and DSC analysis. The authors showed that the unfreezable water was found about 19% of moisture content, but using NMR they found a high water mobility in a region between 9 and 20% of moisture content. According to their results also unfreezable water could show high mobility.

Kou et al. [88] studied the state of water in starch gels and they found different components associated with starch and water, respectively. Richardson [89] showed three different components of water mobility associated in starch. Le Botlan et al. [90] found two components in intact starch correspondent to bound and unbound water.

Cornillon [91] studied the effect of osmotic dehydration treatment on water mobility of apple pieces. In particular, he showed that two peaks, corresponding to different levels of water availability, could be observed after 1 h of soaking, when a sucrose solution of 63% were used. Moreover, he showed that the osmotic dehydration dramatically reduce the water mobility of tissues and thus its availability for chemical reactions.

Evans et al. [92] compared osmotic and air dehydration in strawberry slices by MRI technique. They showed that in a short time of osmotic treatment, differences of T2 values were not significant respect to the control. This observation led to the idea that diffusivity of water from centre to edge of the slice was fast enough to replenish water lost from the surface of samples. Pitombo et al. [93] studied the water profile of Pintado fish in different environmental conditions. The authors showed that at the GAB monolayer value the water exhibits high mobility such as present in capillary ducts and thereby it is available for reaction degradation and microbial growth. Tsai et al (2004) studied the effects of water mobility on anthocyanin degradation in sample of Roselle. They showed that the anthocyanin degradation index was negatively correlated to relaxation rate and positively with water activity values.

All these papers start from the common assumption that spin-lattice and spin-spin relaxation time are a water mobility index, but it is well known that T1 and T2 values are rotational motion indexes rather than translational ones. Water could be considered as a mean in which chemical compounds can react only after a long or short translational motion.

By NMR and MRI techniques, the translational motion of water can be measured, using PFG (pulse-field gradient) experiment (figure. 18).

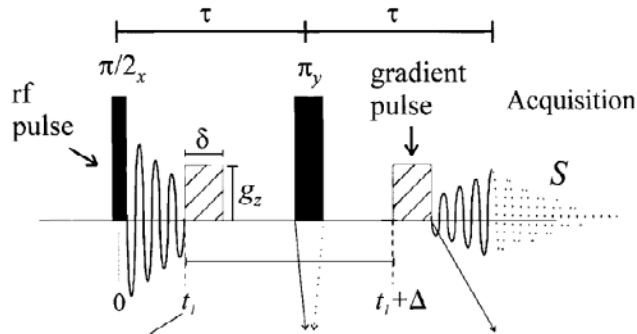


Figure 18. Schematic representation of PFG experiment [from 94]

where g_z and δ are the magnitude and the time of application of gradient respectively. The first pulse ($\pi/2$) labels the initial position of the spin and the second (π) measures the displacement that occurred during acquisition time. If the spins did not move during the acquisition time (Δ) we record a maximum signal; if the spins moved, the intensity of signal reduced (figure 19)

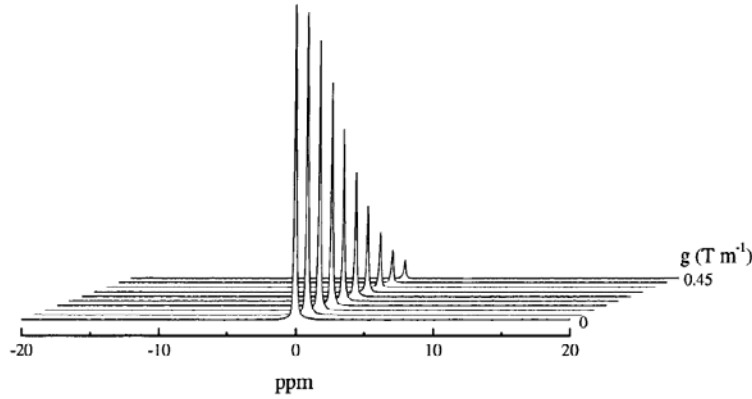


Figure 19. schematic representation on signal decay [from 94].

The equation that correlate the translational motion with the signal is:

$$E = \frac{S(2\tau)}{S(2\tau)_{g=0}} = f(\delta, g, \Delta, D).$$

where g is magnitude of gradient, δ is time application of gradient, Δ is time between the first and second gradient and D is diffusion coefficient. In this way it is possible to calculate the diffusion coefficient of water in different conditions and in different food products.

An exhaustive explanation of the theory can be found by Price [94] and McCharty [95]. Most of scientific papers have been focused to study molecular transport in biological cells, lipid membrane and other areas of research. Benga et al. [96] measured the water coefficient diffusion in blood cells from different species of animal by using PFG-NMR. Anisimov et al. [97] studied the water coefficient diffusion in cotton fiber and Zakhartchenko [98] measured self-diffusion of water and oil in peanuts. Lee et al. [99] studied the self-diffusion behaviour in microorganism using PFG-NMR. They showed that three different components of diffusion, called D_{s1} , D_{s2} and D_{s3} , recorded in *Chlorella* cells could be related to different states of water. Hills et al. [100] studied the change in subcellular water compartmentation of apple tissues. They showed that three different peaks, in terms of relaxation time, can be observed at 800, 400 and 80 ms respectively, which can be assigned to water in the vacuolar, cytoplasm and cell wall compartments. In the same study the authors showed that, during air drying treatment, cells firstly lost water from the vacuole.

Hills and Snaar [101] proposed a cellular model in which three different diffusion coefficients, relative to valcuole (D_1), cytoplasm (D_2) and cell wall (D_3), could be defined; then, another two for plasmalemma membrane (D_{m1}) and tonoplast membrane (D_{m2}) were found. Besides, the membrane are characterized by different width and thus by different permeability coefficients (P).

5.1. Effects of Mobility Water on Osmodehydrated Apples: Preliminary Experiments

On the base of the debate about dynamic and thermodynamic theory we would like present some preliminary experiments regarding the effects of osmodehydration in salt and sucrose solutions on water mobility. In particular figures 20 and 21 show a comparison between a_w values and T2 spin-spin relaxation time of osmotically dehydrated apple samples in sucrose and sodium chloride solutions, respectively.

It is interesting to observe that in both cases T2 reduced very fast compared to water activity, proving that it is likely to obtain food with high water activity but low water mobility. Moreover, a_w value and T2 decreased very fast in salt rather than sucrose solution. This difference could be explained by different ways. First, the big size of sucrose molecules, compared to sodium and chlorine ions, could hinder the flow across cell membrane, after their dissolution in water; as a results, an high content of salt molecules in cell tie water more than sucrose. Secondly, sodium chloride is a cell compatible solute, able to cross cell membrane, reaching the internal part of vacuole, that is a compartment very rich of water. Despite, sucrose can flow only across cell wall, being able to dehydrate vegetable tissue only in one section of cells. Moreover, sodium and chlorine ions interact with water by strong electrostatic bonds, compared to the hydrogen bonds formed between sucrose and water.

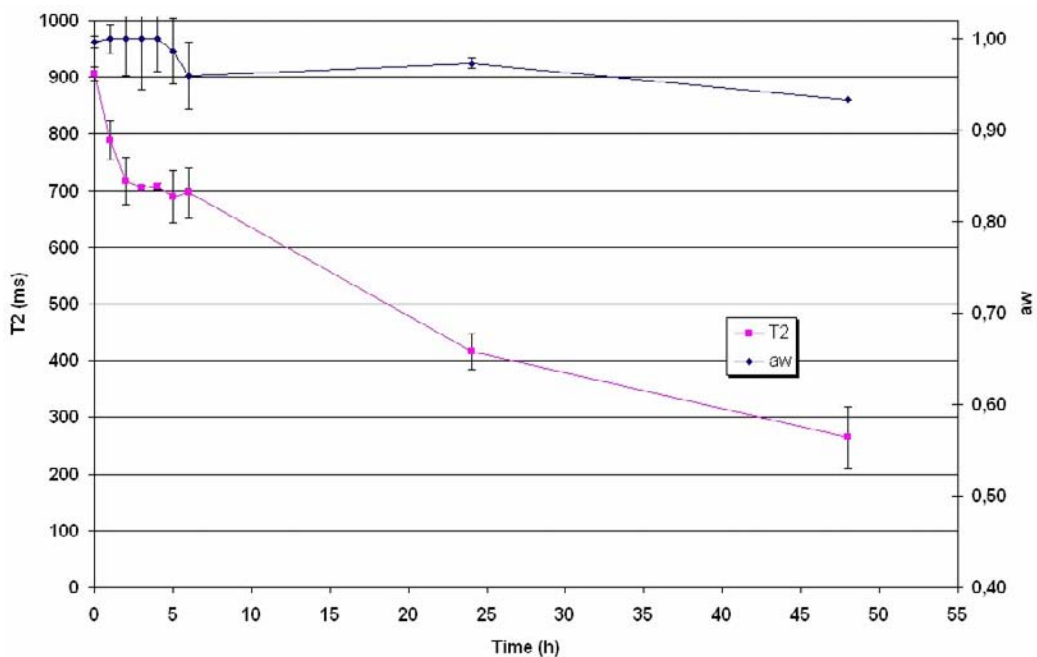


Figure 20. Trend of a_w and T2 values as a function of treatment time of osmotically dehydrated apple samples in sucrose solution.

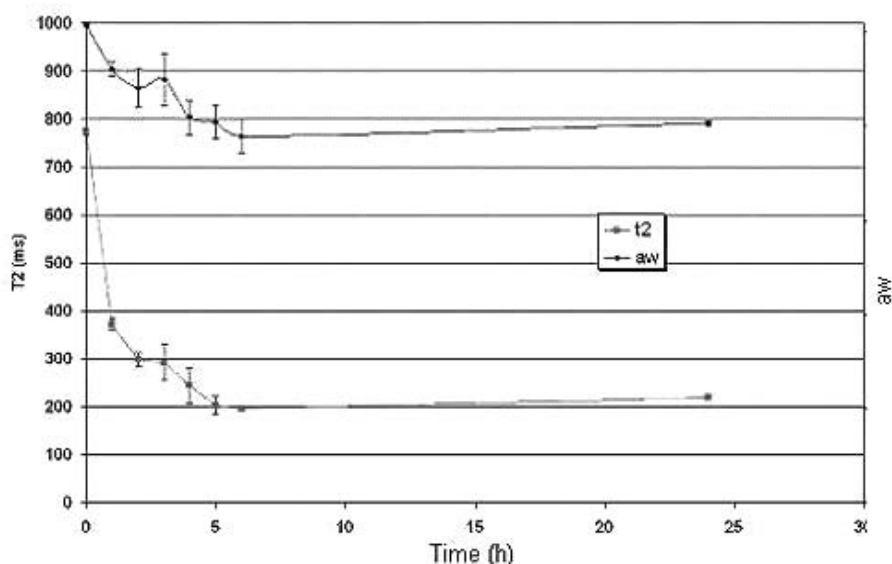


Figure 21. Trend of a_w and T2 values as a function of treatment time of osmotically dehydrated apple samples in NaCl solution.

Apple osmotically dehydrated in sucrose solution showed water activity values almost constant; in fact values did not significantly change in the first 5 hours and then a_w began to slowly decrease until 0.93, after 48 hours of treatment. Despite, T2 values showed a different trend. According to Cornillon [90] we observed a significant reduction in the first 6 hours of treatment from 900 to 700 ms. Later, spin-spin relaxation time kept on a slow reduction, reaching 417ms and 264ms after 24 and 48 hours of soaking time respectively. For samples submitted to osmotic dehydration in salt solution, the change in terms of water activity and T2 values were fast. Already after one hour of treatment a_w value reduced from 1 to 0.92 and after six hours of soaking time, value reached 0.78. Moreover, in the first six hours of experiment, T2 spin-spin relaxation time reduced from 773 to 197 ms.

Conclusion

Water availability for chemical degradation reactions and microbial growth is the most single important parameter for stabilization of food. Since researchers have recognized the importance of the availability of water rather than the moisture content, water activity was used as index to measure the state of water in food. Despite these considerations it is possible to state that the techniques of water activity modulation in food are, nowadays, still few.

Theoretically, the possibility to bond water, reducing its availability, is, maybe, the best idea to stabilize food, when water content and textural properties (plastizicing effect) are kept, without reducing organoleptic and nutritional quality. Practically, the poor knowledge relative to the interactions between ingredients, the use of humectants, the mechanisms of mass transfer during air dehydration processes, osmotic dehydration and also during storage, have not allowed up till now the wide application of this idea. Another hurdle of the wide use

of modulation of water availability, as stabilization process, is the difficulty to predict a_w values in real complex food.

We studied the possibility to obtain the partial stabilization of pesto sauce by a_w reduction. The results showed that, in our conditions, starting to fresh basil the threshold of 10^5 cells/g was not reached and sample kept a colour overlapped to raw material.

Also, a combined treatment of a_w and pH reduction, by a easy planned addition of humectants and lactic acid, was found effective to obtain pH and a_w values under the threshold useful for microbial growth.

A easy empirical model to predict a_w values in vegetable creams was obtained. In particular the proposed equation was directly correlated with percentage of humectants, resulting enough flexible to plan the addition of salt or sugar, with the aim to obtain products with the desired taste features. The validation of equation on aqueous solution, extract aqueous and mushroom creams stated its capability to predict a_w values with high accuracy. In the same way, if we added olive oil to mushroom creams or if changed raw material (apple rather than mushroom), the equation was able to forecast a_w with high precision.

In the last 20 years water activity has been object of several criticisms. In particular, the interest of food scientists on a new theory based on dynamic rather than thermodynamic has been increased. Water is thought as unavailable if cannot move in food; then, with a very high viscosity (or low mobility) of the medium, reactants are unable to move and to react.

Theory recognizes the importance of T_g value as an index of processability, quality and safety of food; nevertheless, the obtained results are contradictory and the poor available knowledge do not allow us to indicate a common behaviour of the most important degradation reactions as a function of water mobility. Often, the meaning of term “water mobility” is not in accordance among different authors.

In this area, a lot of question are still open and we are far to well explain the relation between state of water and food stability.

For instance, as reported above, several authors supposed that the first parts of Maillard reaction could occur inside the holes of model systems obtained by freeze-drying, but results were not always in accordance. With an accurate study of literature we observed that model systems were prepared by different conditions of freeze-drying, like freezing temperature, pressure and time process. So, we should expect different hole's size and shape, because the correlation between size and shape of holes of freeze-dried products and process variables is well known. We think that these differences could be one of reasons to explain the results. This aspect was always neglected in the discussion of results.

Also, next questions need as soon as possible answers:

- a) Is it possible to think T_g values as a non-perfect threshold but as a continuum change in viscosity and mobility water from $T_g - T_i < T_g < T_g + T_i$?
- b) As water activity increases and T_g decreases, is it possible to think that dilution effect becomes more important rather than viscosity effect, for the decrease of degradation rate (as shown in figure 17)?
- c) How much the reactivity of chemical compounds can affect the results?
- d) How much the correct direction for the collision between two different chemical species can affect the rate constant of reaction itself?

NMR techniques gives us the possibility to measure indexes of rotational mobility of water (T2 and T1) and also the translational diffusion coefficient (D), but more knowledge are necessary all the same to modulate the mobility water with the aim to control the food degradation reactions.

If is a common assumption that the mobility water can lead all chemical reactions, very few scientists have focused on this problem. The questions that we would like submit are the following:

- a) Is it possible to relate the rate of degradation reaction of food to water diffusion coefficient?
- b) Is it possible to define a water diffusion coefficient threshold, over that the different chemical reaction exhibit a higher rate?
- c) Which is the connection between water diffusion and microbial growth or toxin production?
- d) If we have two different components of water ("free" and "bound"), is it possible manipulate their relative content in food?
- e) How the common industrial processes (osmotic dehydration, air dehydration, microwave dehydration, addition of different humectants, heat treatment, etc.) can modify the translational motion of water? What occurs in terms of water transfer during this treatment? How the water moves inside the food during industrial treatment?
- f) What occurs during storage time in terms of mass transfer inside the food and between food and environment?

All these question need the answer in next years. Only with further knowledge in this area good results, in terms of control of food quality, could be achieved, with the aim to obtain a long shelf-life of food, without applying strong stabilization treatments.

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Chapter 3

NATURAL ANTIOXIDANTS FROM AGRO-FOOD BY-PRODUCTS: AN EXPERIMENTAL APPROACH FOR RECOVERY OF PHENOLICS FROM WINE-MAKING BY-PRODUCTS

***Giorgia Spigno, Lorenza Tramelli
and Dante Marco De Faveri***

Institute of Enology and Food Engineering – Università Cattolica Sacro Cuore,
Via Emilia Parmense, 84 – 29100 Piacenza – Italy - giorgia.spigno@unicatt.it

Abstract

This chapter is aimed to underline the increasing importance that natural antioxidants have been gaining in the last years. Antioxidants are naturally present in many foods, so that they can be seen as potential recovery sources: oilseeds, nuts, cereals, legumes, vegetables, fruits, herbs, spices and teas. Besides these, antioxidants are often present in food processing by-products and wastes, so that the employment of low-cost industrial wastes could greatly reduce the production costs and increase the margin profit of the products. The introductory section summarises the classes of antioxidant compounds (mainly focusing on phenolic compounds), their potential food and no-food applications, and the main problems you have to account for when recovering antioxidants from residual sources, such as selection of a suitable agriculture by-product, choice and optimisation of the extraction procedure, analytical characterisation and evaluation of antioxidant activity of the obtained extracts, evaluation of potential applications of the isolated substances.

The second part of the chapter presents an experimental work dealing with recovery of phenolic compounds from wine-making wastes through a simple solvent extraction process. Trials were carried out in order to evaluate the feasibility of using different by-products (grape stalks, grape marcs before and after distillation), the influence of grape variety, of different sample pre-treatments, type of solvent, extraction temperature and time (extraction kinetics) on extracts yield and quality in terms of phenolics content and antioxidant power. Food applications of the obtained compounds to inhibit oil oxidation and to extend shelf-life of fresh fruits were also investigated.

Introduction

The importance of the antioxidants contained in foods is well appreciated for both preserving the foods themselves (especially fats, oil and fat containing food products), for preventing deterioration of other oxidisable goods, such as cosmetics, pharmaceuticals and plastics, and supplying essential antioxidants *in vivo*. Since synthetic antioxidants, such as BHA and BHT, have restricted use in foods due to their toxicological effects on various species and suspected carcinogenic potential, the search of natural and safe antioxidants, especially of plant origin, has greatly increased in recent years. This, together with the fact that antioxidants are naturally present in many foods (oilseeds, nuts, cereals, legumes, vegetables, fruits, herbs, spices, teas and meat) [65], explains why scientific literature about natural antioxidants has been proliferated so much.

When dealing with recovery of natural antioxidants, different aspects and problems should be considered and faced off: choice of a suitable extraction source; classes of compounds you are interested in for extraction; optimisation of the extraction procedure; chemical analysis of the extracts and evaluation of their antioxidant power; application of the extracts.

This chapter aims to summarize all these aspects, underlining the great opportunity of exploiting agricultural and industrial wastes for recovery of antioxidants (in particular phenols), and presenting a case-study related to the extraction of phenolic compounds from wine-making wastes [90, 93].

Classes of Natural Antioxidants

Natural antioxidant definition includes different chemical compounds, such as tocopherols, carotenoids, phenolic compounds, amino acids, peptides, protein hydrolysates, phytates, phospholipids, vitamins and enzymes [82].

Among the most important groups of natural antioxidants are the tocopherols, flavonoids and phenolic acids.

Tocols

Tocols can be classified as either tocols or tocotrienols (Figure 1); within each of these two classes there are four isomers (α , β , γ , δ), making a total of eight tocols.

Tocols can act as antioxidant by two primary mechanisms: a chain-breaking electron donor mechanism and a chain-breaking acceptor mechanism. The second is the major and includes singlet oxygen scavenging or quenching. The antioxidant power (AOP) is strongly concentration dependent, but at high concentration a pro-oxidative effect can be observed. Tocols are very stable with respect to heat.

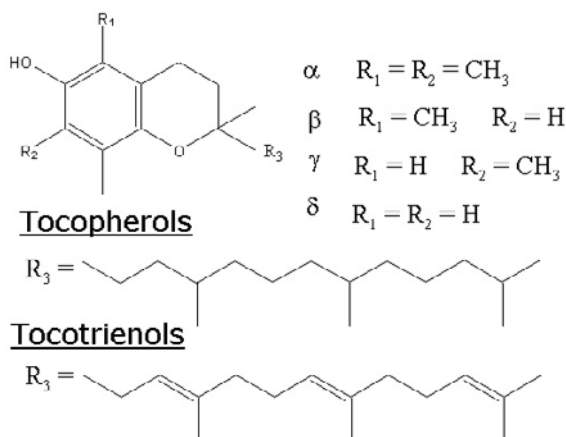


Figure 1. Chemical structure of tocols.

Carotenoids

Like tocopherols, carotenoids (Figure 2) are also effective singlet oxygen quencher, with the rate of quenching depending on the number of conjugated double bonds: a conjugated chain with seven or fewer double bonds is not able to delocalize the unpaired electrons gained from the singlet oxygen.

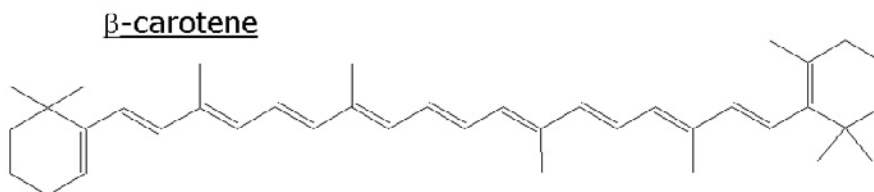


Figure 2. Chemical structure of a carotenoid.

Phenolic Compounds

Phenolic compounds are ubiquitous in plants, where they play an important role in growth and reproduction, providing protection against pathogens and predators, besides contributing towards the colour and sensory characteristics of fruits and vegetables [8]. Structurally, phenolic compounds comprise an aromatic ring, bearing one or more hydroxyl substituents, and range from simple phenolic molecules to highly polymerised compounds, even though the group is often referred to as “polyphenols”. Most phenols naturally occur as conjugates with mono- and polysaccharides, linked to one or more of the phenolic groups, and may also occur as ester and methyl ester derivatives. They can be categorised into the following classes: simple phenolics, benzoquinones (C_6); hydroxybenzoic acids ($\text{C}_6\text{-C}_1$); acetophenones, phenylacetic acids ($\text{C}_6\text{-C}_2$); hydroxycinnamic acids, phenylpropanoids ($\text{C}_6\text{-C}_3$); naphthoquinones ($\text{C}_6\text{-C}_4$); xanthenes ($\text{C}_6\text{-C}_1\text{-C}_6$); stilbenes, anthraquinones ($\text{C}_6\text{-C}_2\text{-C}_6$); flavonoids, isoflavonoids ($\text{C}_6\text{-C}_3\text{-C}_6$); lignans, neolignans [$(\text{C}_6\text{-C}_3)_2$]; biflavonoids [$(\text{C}_6\text{-C}_3\text{-C}_6)_2$];

C₆)₂]; lignins [(C₆-C₃)_n]; condensed tannins (proanthocyanidins or flavolans [(C₆-C₃-C₆)_n]). Figure 3 reports the structure of only some phenolic compounds, as an example.

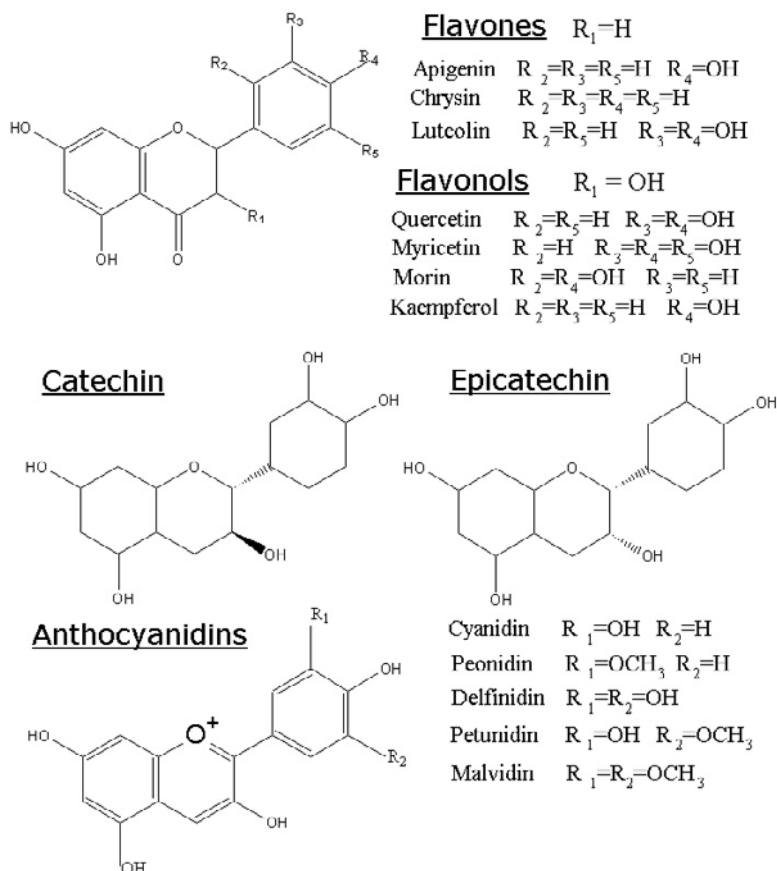


Figure 3. Chemical structure of some phenolic compounds.

The antioxidant activity of phenolic compounds is due to their ability to scavenge free radicals, donate hydrogen atoms or electron, or chelate metal cations, with a strong structure-activity relationship [8, 43, 48, 52, 75].

Amino Acids, Peptides

Amino acids and peptides (in particular histidine-containing peptides) are typical metal-chelating agents frequently present in foods and found in abundance in protein hydrolysates [82].

Phytates, phospholipids, vitamins and enzymes

Phytates are strongly negatively charged compounds, the antioxidant activity of which is presumably due to chelation of prooxidant metal ions [82].

Phospholipids are obtained as by-products of oil-refining (especially from soybean) and are known to affect lipid oxidation.

Fat-soluble vitamins, such as vitamin E and vitamin A, and water soluble vitamins such as vitamin C as well as β -carotene (vitamin A precursor) are known to exert antioxidant activity [104].

Enzyme antioxidants include superoxide dismutase, catalase, glutathione peroxidase and reductase, glutathione-S-transferase and phenol oxidase [108].

Natural Antioxidants from Residual Sources

Literature is so rich of examples of recovery of antioxidant compounds from natural sources, that it is not possible to report here a complete list of them. This abundance of literature is due to the fact that antioxidants are naturally present in many foods, so that they can be seen as potential sources of natural antioxidants: oilseeds, nuts, cereals, legumes, vegetables, fruits, herbs, spices, teas, meats, trees and the different parts of the plants such as leaves, roots, hulls, sprouts and seeds [65, 82].

On the other hand, the processing of foods results in the production of by-products that are rich sources of bioactive compounds, including phenolic compounds which are also responsible for the adverse impact of many food industries. In industrial wastewaters, in fact, these compounds considerably increase biochemical and chemical oxygen demands, with detrimental effects on the flora and fauna of discharge zones, while in solid residues used as fertilizers, they may inhibit germination properties. Since in the last few years diminishing the environmental impact of industrial wastes has been a subject of increasing concern, recovery of phenolic compounds (which can be considered as high-added-value by-products for their antioxidant properties) from low-cost industrial wastes could be a great opportunity to reduce the production costs, increase the margin profit of the products and valorise the wastes reducing their polluting character.

Among the many investigated residual sources of antioxidants we can remember: cereal hulls, dried fruit hulls, peel and seeds of several fruits, the by-products of the olive industry, shrimp shell waste, and protein hydrolysates [8, 52].

Application of Natural Antioxidants

Phenolic compounds and antioxidants in general, have been reported to exert favourable effects on human health such as protection against cardiovascular disease, anti-inflammatory activity and anti-carcinogenic effects [23, 35, 38, 41, 83, 100, 103]. The pharmacological actions of phenolic antioxidants stem mainly from their free radical scavenging and metal chelating properties as well as their effects on cell signalling pathways and on gene expression. That's why traditionally, natural antioxidant extracts have been thought for a medical use, but since there are still many uncertainties about their effective bioavailability and metabolism [7, 34], it appears really interesting and promising their application in food systems.

Some studies have investigated the addition of natural antioxidants to vegetables oils to inhibit oxidation during storage [9, 13, 96] or during frying [42, 47]. Natural antioxidants have also been added to inhibit lipid oxidation in meat [10, 80] and biscuits [72], to preserve the endogenous antioxidant system of fish muscle [59], or to preserve fresh beef meat colour

by incorporating them into packaging polyethylene films [51]. The prerequisite is, of course, that the added natural compounds do not alter either the flavour or aroma of the food.

Furthermore, natural antioxidants are often used as ingredients or additives of both human and pet foods and of cosmetic products (body creams, sun protection creams, etc.).

Recovery of Natural Antioxidants

Different technologies are available for the extraction of secondary metabolites, such as phenolic compounds, from plant material [94]: solvent extraction, steam extraction, supercritical extraction [33, 56, 86, 105], high pressure extraction [30].

Solvent-extraction is the most commonly performed procedure but, at present unambiguous data on the methods and conditions for extraction are available and sometimes contradictory, particularly if different raw materials are considered. Moreover, results are difficult to compare even because phenols are measured in different ways and sometimes only the phenolic content of the final extracts is reported, but not the total yield. The aim of an extraction process should be, of course, to provide for the maximum yield of substances and of the highest quality (concentration of target compounds and antioxidant power of the extracts). However, the choice of operating parameters is often not motivated, even because many researches are simply aimed to analyse the phenolic content. Spigno et al. [90] tried to compare and summarize the different extraction procedures used for antioxidant recovery from different natural sources, in terms of phenols yield and content in the final extracts, and in terms of the optimisation of some process parameters. The variables to account for in process optimisation are many, so that it is not easy to optimise all them together, and often literature lacks of systematic approaches to optimise the process in order to maximise the extract yield, purity and antioxidant power of the obtained extracts [4, 52, 99]. Beside the process parameters, one must also take into account the difficulties related to the analysis of the extracts, and to the evaluation of the antioxidant power.

First of all the raw material should be selected on the basis of its potential antioxidant content, of its availability in sufficient amount, and of course of its cheapness.

Storage conditions, mincing and degreasing are among the most investigated pre-treatments of raw materials. For storage purpose, the sample can be dried, frozen or vacuum packed, or exposed to a combination of these techniques. In any case, the conditions employed should be as mild as possible to avoid oxidation, thermal degradation and other chemical and biochemical changes in the sample. Reduction of particle size should increase the superficial area available for mass transfer and, then, increase extraction yield, while degreasing might help removing interfering compounds and increasing extract purity.

Both extraction yield and antioxidant activity of extracts are strongly dependent on the solvent, due to the different antioxidant potential of compounds with different polarity. Ethyl-acetate and aqueous methanol or alcohols are often the solvents of choice for recovery of a wide range of phenolics from different sample types. Ethanol and water are the most widely employed solvents for hygienic and abundance reasons, respectively, but they are not selective and bring inevitably to the concomitant extraction of other substances. Anyway, depending on the starting substrate and on the target compounds, selection of the optimal solvent providing maximum antioxidant activity and yield should be achieved after accurate review of the available literature, and by means of comparative studies [52, 99]. Working in

an inert atmosphere and away from light, would greatly prevent oxidation of phenolics, and addition of antioxidant compounds such as ascorbic acid and SO₂ has been proposed for the same purpose [81].

Temperature and time are two other key process variables in solvent extraction. From a pure mass transfer point of view, temperature increase favours extraction by increasing solubility and diffusion coefficient of any substance. On the other hand, temperature affects the compound stability due to chemical and enzymatic degradation, losses by volatilization or thermal decomposition. In addition to thermal decomposition, phenols can react with other plant components, impeding their extraction, and prolonged exposure at moderate temperatures can also cause phenolic degradation [52]. There are also opposite results showing a positive effect of temperature on antioxidant activity of natural phenols [63]. A detailed kinetic investigation should be required for selection of the best time/temperature combination.

Ultrasound and microwave assisted solvent extractions (UAE and MAE) have also been successfully applied for the extraction of bioactive principle from plant materials. UAE has become a good alternative to classical extraction methods due to its high efficiency, low energy and water consumption (no reflux or refrigeration are needed). The enhancement on extraction is attributed to the disruption of the cell walls, reduction of the particle size and the enhancement on the mass transfer of the cell content to the solvent caused by the collapse of the bubble produced by cavitation [77, 97, 103]. MAE is based upon the selective and rapid localized heating of moisture in the sample by microwaves. Due to the localized heating, pressure builds up within the cells of the sample, leading to a fast transfer of the compounds from the cells into the extracting solvent. MAE can globally reduce solvent amount, and/or enhance extraction efficiency, and reduce working time [31, 57, 68, 78].

The final extracts must then be stored before their employment, investigating the stability and shelf-life as a function of storage conditions, where temperature, light and atmosphere are again the major factors influencing antioxidant activity.

Characterization of Antioxidant Extracts

In order to assess the efficiency of the adopted extraction procedure and the influence of the varied parameters, evaluation and quantification of both phenolic compounds and antioxidant power are needed.

Chemical analysis can be qualitative and/or quantitative. Unless a specific target substance is looked for, it is almost impossible to get a complete characterization of all the extracted phenols, because it is very difficult to possess the standards for the thousands of known phenols, even if, of course, depending on the natural source, this number can be greatly narrowed. Chromatographic methods (high performance liquid chromatography, gas chromatography eventually in combination with mass spectrometry) are the best methods for phenols identification and quantification because generally free of interference, but, as already underlined, they require appropriate standards [4, 76]. On the contrary, traditional methods have relied on direct measurement of absorption of radiation in the ultraviolet (for example 320 nm for cinnamic acids, 360 nm for flavonols, 280 nm for other phenols, 520 nm for anthocyanins) or, more commonly, on colorimetric methods using Folin-Ciocalteu reagent, which, however, is not specific for phenols because it reacts with any reducing

substance undergoing interferences with many other compounds such as sugars and proteins [24]. Another limit of these methods is that a commonly occurring phenolic depending on the analysed class must be selected (often gallic acid for total phenols, caffeic acid for cinnamic acids, quercetin for flavonols, malvidin for anthocyanidins, and so on), so that results are expressed in terms of molar equivalents, and this can be a problem particularly where there is not a single class of phenolics predominating. The spectrophotometric methods usually overestimate the phenols content compared to chromatographic methods. On the other hand, when a process optimisation study is being carried out, determination of total phenols, or of some classes of phenols, can be enough, and colorimetric analyses are decidedly more time and cost saving than chromatographic ones.

As it concerns the evaluation of antioxidant activity, although there is a great multiplicity of used methods, there are no approved, standardised methods [25, 66, 67, 95]. Since several rapid screening test methods and *in vitro* antioxidant protocols have been published and used, the data obtained by different researchers are extremely difficult to compare and interpret, due to the variability of experimental conditions and differences in physicochemical properties of oxidizable substrates. Mechanisms of antioxidants action can be multiple and they become more complex in real foods and biological systems respect to model systems; therefore valid evaluation of antioxidant activity should require the use of several different assay methods. From a comparison based on simplicity, instrumentation required, biological relevance, action mechanism, and application on lipophilic and/or hydrophilic substrates, three methods were proposed as the best ones [67]: the ORAC assay (oxygen radical absorbance capacity), the TEAC (trolox equivalent antioxidant capacity) or other ABTS radical based assays; and the Folin-Ciocalteu antioxidant capacity or total phenolic assay. The important thing is, whichever method is chosen, to bear in mind all its associated limits and disadvantages.

A Case Study: Recovery of Phenolic Compounds from Wine-Making by-Products

Grapes are one of the world's largest fruit crops, and even wine-making wastes such as marc (the residue after pressing for white wines or vinification for red wines) and stalks, are rich in phenols.

Most of the published references concerning antioxidant recovery from grape started from fresh raw material, rather than from wastes, as is the case for works which utilized directly whole grape [2, 73], grape seeds or skins [1, 11, 37, 56, 64, 81, 88]. However, the number of papers related to the use, or potential use of wine-making wastes, such as grape marc or stalks, has been increasing in the last years [14, 17, 18, 29, 36, 44, 53, 60, 89, 98].

Almost all the cited works used a solvent-extraction procedure [90], where the choice of operating parameters was not always motivated, and only a few studies were aimed to parameters optimisation. The most investigated factors up to now have been: crushing and drying pre-treatments; type of solvent; solvent/sample ratio; time and temperature of extraction.

As it concerns sample pre-treatments, degreasing was applied to grape seeds, which contain about a 13-20% lipids, without comparing results obtained from un-degreased samples [11, 36, 37]. As already commented, reduction of particle size should increase the

superficial area available for mass transfer and, then, increase extraction yield. However, size obtained after powdering of the sample was not always specified. Some authors [14] reported a higher extraction of phenolic compounds by acting on crushed than on uncrushed marc, but crushing details were omitted. Other authors [60] wrote that grinding of grape seeds could shorten the extraction time but did not increase the yield of proanthocyanidins, and, furthermore, caused a significant increase in the extraction of undesired concomitant components, so they used entire grape seeds, such as [3]. In [61] it was investigated the effect of different particle size in a continuous phenol extraction, and they concluded that a higher amount of total polyphenols was obtained with the lower flow rate, sample amount and particle size. Actually, the authors expressed the yield as an index of $\text{mg phenols l}^{-1} \text{ h}$ (the area under the polyphenols concentration curve as a function of time), but if these values are transformed into the yield of polyphenols ($\text{mg phenols/mg of sample}$), that is to say taking into account the solvent flow rate, very similar results for the different tested particle size of 0.5 and 5 mm are obtained.

The effect of the solvent/sample ratio has been investigated by [61] and by other authors for different raw materials [15, 32]: the higher the ratio, the higher the total amount of solids obtained, despite the solvent used, according to mass transfer principles.

Type of solvent has been the most investigated factor. Ethylacetate was reported as one of the best solvent for extraction of polyphenols from grape seeds (it is capable of selectively extracting proanthocyanidins) and water addition up to a certain level (10%) increased proanthocyanidins yield because of increased permeability of grape seeds, but beyond this level significant amount of concomitant substances were extracted [60]. On the other hand, alcoholic solvents have been commonly employed to extract phenolics from natural sources: they give quite high yield of total extract even though they are not highly selective for phenols. Particularly, mixtures of alcohols and water have revealed to be more efficient in extracting phenolic constituents than the corresponding mono-component solvent system [61, 105]. Regarding grape and wine-making wastes, influence of water content of alcohols has been studied only for extraction from seeds [3, 106]. Ethanol (a dietary alcohol) may be preferable than methanol in view of a food application of the extracts. Furthermore, being a polar solvent, it effectively extracts flavonoids and their glycosides, catecols and tannins from raw plant materials [12], but solubility of these compounds can be enhanced using a mixed solvent over a limited compositional range [15].

Time and temperature of extraction are important parameter to be optimised even in order to minimise energy cost of the process. Many authors agree in the fact that an increase in the working temperature favours extraction enhancing both the solubility of solute and the diffusion coefficient, but also that beyond a certain value phenolic compounds can be denatured [62, 105]. More contradictory are the data available for extraction length: some authors chose quite short extraction times [14, 62, 106]; other quite long times [37, 44, 60, 61].

Since, generally, we have noticed that literature lacks of systematic approaches to optimise the process in order to maximise the extract yield, purity and antioxidant power of the obtained extracts, the aims of our studies were to:

- Investigate extraction of antioxidants from two wine-making wastes, marc and stems. Unlike marc, stalks have never been studied for this purpose. For better comparison marc and stalks were collected from the same grape variety and vintage. Then,

possibility of using distilled marc, and influence of grape variety and vintage were also investigated.

- Simplify the extraction procedure. On the basis of published researches, a solvent extraction method was selected and the influence of some process parameters on the final extract yield, phenolic content and antioxidant power was evaluated: degreasing pre-treatment of the material, type of solvent (ethylacetate, ethanol, and aqueous ethanol), extraction time and temperature; freeze-drying of extracts.
- Investigate food application of extracts: inhibition of oil oxidation, and extension of fresh strawberry fruits shelf-life were considered.

Materials and Methods

Materials

Stalks and marc (by Barbera red grape) were kindly provided by a wine-making factory in Piacenza (northern Italy). Stalks were collected after the operation of pressing/destemming, while marc was collected after devatting. Both the materials were oven dried at 60°C up to a moisture content of about 2-4% (determined by dry weight in oven at 105°C until constant weight) and milled through a 2 mm sieve (final powder size ≤ 2 mm). Marcs by mixed red and white grapes were collected before and after distillation from a distillery in Piedmont (northern Italy).

All chemicals were of analytical grade. β -carotene, linoleic acid, BHA, Tween 40, gallic acid, caffeic acid and Trolox® were supplied by Fluka. Folin-Ciocalteu reagent was purchased from Merck, quercetin, ABTS and PVPP (polyvinylpolypyrrolidone) from Sigma-Aldrich Chemie GmbH.

Extraction of Phenolic Constituents

In case of degreasing pre-treatment, samples were degreased in a Soxhlet apparatus with hexane for 6 h in the case of stalks, and up to 24 h in the case of marc.

Dried and milled sample was extracted with the solvent in a thermostatic rotary shaker at 80 rpm (Infors AG, CH-4103 Bottmingen/Switzerland) with a 4/1 (v/w) ratio solvent/sample (wet weight of oven dried marc). The liquid extract was separated from solids by centrifugation (5350g for 5 min, ALC 4237R centrifuge). In the first set of trials, the liquid phase was then dried over anhydrous Na_2SO_4 , and solvent was removed by evaporation under reduced pressure at 40°C. Petroleum ether was added to the concentrated (in ratio 5:1) to form a precipitate which was separated by centrifugation [60, 64]. The residue (crude extract) was dissolved in ethanol for freeze-storage and analysis.

In the second set of trials the liquid phase was directly analysed and freeze-dried, repeating the analyses on freeze-dried samples in order to assess any influence of this operation.

The first trials were aimed to the evaluation of suitability of marc or stalks as phenols sources, of ethanol or ethylacetate:water/9:1 as solvent, 5 or 24h as extraction time, 28°C or 60°C as extraction temperature. All the 32 resulting combinations (4 parameters, each one made varying on two levels) were performed at least in triplicates.

The mixture ethylacetate:water was selected since being reported as one of the best solvent for extraction of polyphenols from grape seeds [60], because it preferentially extracts those phenols that are readily dissolved in the lipid fraction of the food, because its low boiling point facilitates its removal and reuse and, finally, because any possible residue is scarcely toxic since at levels around mg/l it is a typical component of fermented drinks [14]. Ethanol was chosen since alcohols are the most used solvents in antioxidants extraction works and, furthermore, it is the natural solvent of these compounds in the wine-making process. 28°C was selected to simulate a room temperature, 60°C was chosen as the upper limit for hot extraction since it is reported that polyphenols are heat sensible [15]. The extracts were characterised for total phenols content, and antioxidant power (β -carotene-linoleate system).

The next set of experiments was aimed to optimise the extraction of phenolic compounds from grape marc investigating extraction kinetics (from 1 to 24 h) at 45°C and 60°C, and the effect of water addition to ethanol on phenols yield and quality of extracts (phenols concentration and composition, and antioxidant power). All the extraction trials were carried out in triplicate.

For each phenolic class, yield and extract concentration were calculated as:

Yield (%): $g_{phenols} / 100 g_{dried\ marc\ (dry\ weight)}$

Phenols content or Purity (%): $g_{phenols} / 100 g_{freeze-dried\ extract}$

Total extract yield (%): $g_{freeze-dried\ extract} / 100 g_{dried\ marc\ (dry\ weight)}$

Chemical Analyses

Total Phenols

Total phenols were determined according with two different methods:

- 1) Folin-Ciocalteu [74]. This method was used since it is the one adopted in almost all the published works about natural antioxidant recovery, being considered the best method for total phenolics (including tannins) determination [22].
- 2) Direct reading of the absorbance of the sample at 280nm [74]. This a faster procedure based on the absorbance of the aromatic ring. Most catechins have a maximum absorption at around 280nm, (+)-catechin is reported to be the major catechin monomer in all grape skins and total phenols and tannins contents are reported to be highly correlated with absorbance at 280nm [106].

In both cases total phenols were expressed as gallic acid equivalents (GAE) by means of calibration curves with standard gallic acid.

Tannins

The applied analytical method (acid butanol assay) is based on the ability of monomer and condensed 3-4, flavandiols to oxidise in acid and alcoholic medium at high temperature to give coloured procyanidins. Tannins were calculated by comparison with a standardised oligomeric procyanidin solution [74].

Percentage of tannins on total phenols was estimated by the polyvinylpolypirrolidone (PVPP) method [49] which is based on the fact that PVPP binds tannins. 1 ml of distilled water is added to 100 mg PVPP and vortexed with 1 ml of extract. The mixture is kept at 4°C for 15 min, vortexed again and centrifuged. The supernatant has only simple phenolics other than tannins, so the difference between total phenols before and after the PVPP treatment gives the tannin fraction.

Anthocyanins

Free anthocyanins and anthocyanins combined with tannins were measured through a chemical method based on their specific properties of bleaching by SO₂, and calculated by comparison with a standardised anthocyanin solution [74].

Cinnamic acids and flavonols

Cinnamic acids were determined by reading absorbance of the sample at 320nm and expressed as caffeic acid equivalents (CAE) through a calibration curve [19].

Flavonols were determined by reading absorbance of the sample at 370nm and expressed as quercetin equivalents (QE) through a calibration curve [19].

Antioxidant power

For the first set of experiments the antioxidant activity of the extracts was evaluated in a β -carotene-linoleate system [37]. 0.2 mg of β -carotene, 20 mg of linoleic acid and 200 mg of Tween-40 were mixed in 0.5 ml of chloroform. After removing of chloroform at 40°C under vacuum, the mixture was diluted with 50 ml of oxygenated water and well mixed. Aliquots of this emulsion (5 ml) were transferred into different test tubes containing 0.2 ml of extracts in ethanol (200 ppm) or 0.2 ml of ethanol (control), or 0.2 ml of BHA (200 ppm; GRAS regulations limit BHA to 200ppm of the fat or oil content of the food product). Absorbances of all the samples were read at 470 nm (holding the samples at 50°C) at 15 min intervals. All determinations were carried out in triplicate. An emulsion prepared as above without β -carotene served as blank. The antioxidant activity index (AAI) was evaluated in terms of bleaching of the β -carotene and calculated as:

$$AAI = \frac{(\Delta A_E - \Delta A_C)}{(\Delta A_B - \Delta A_C)} * 100$$

where ΔA_B is the variation in absorbance (from time 0 to 150') of the sample containing BHA (with assigned AAI = 100); ΔA_E that of the sample containing the extract; ΔA_C that of the blank (with assigned AAI = 0).

For the second set of experiments antioxidant power of the freeze dried extracts was assessed according to the ABTS assay [70], which is based on the ability of antioxidants to interact with the radical ABTS decreasing its absorbance at 734nm. Antioxidant power (AOP) was calculated as percentage inhibition:

$$AOP = \% \text{ Inhibition} = \left(\frac{A_{Blank_{t=6}} - A_{Extract_{t=6}}}{A_{ABTS_{t=0}}} \right) * 100$$

where A_{Blank} was the value of absorbance for the blank (ethanol), $A_{Extract}$ was the absorbance of the extract (dissolved in ethanol), t indicates the time (in minutes) at which absorbance was read.

AOP was also converted into Trolox® equivalents antioxidant activity (TEAC) by a calibration curve obtained with standard Trolox® (1-15µM final concentration in the cuvette). TEAC is the ratio of mM Trolox® to mM phenols in the extract (as GAE).

Food Applications

Inhibition of oil oxidation and extension of shelf-life of fresh strawberry fruits were investigated as potential food applications of the extracts.

As it concerns prevention of oil oxidation, some preliminary tests were carried out according to the *Shaal Oven Test* (or accelerated resistance test) which simply consists in monitoring the increase of peroxides value (PV) [5] in an oil sample kept in a thermostatic oven at 60°C. The addition of antioxidants should avoid or, at least, delay, the peroxides formation. Sunflower oil was bought at a local market. As suggested by [9], calculated amounts of the extracts were mixed with 4 ml of absolute ethanol and added to 25g of oil, and alcohol was evaporated during stirring. Oil samples (25g), without and with antioxidants (200ppm BHA or 200ppm extract) were placed in open flasks and PV measurements were done every two days according to the AOCS method Cd 23-93 [20].

As it concerns extension of strawberries shelf-life, the antifungal activity of phenolic extracts against *Botrytis cinerea* was assessed. Fungi *B. cinerea* were isolated from diseased berries on PDA (potato dextrose agar) by the single spore procedure. Inoculated plates were held at 27°C for 7 days. The cultures were transferred to PDA slants and maintained at 4°C until use. The antifungal assay was determined on PDA plates amended with different extract concentrations. The plates were seeded with 6mm diameter mycelial plugs cut from the edge of 4-day-old *B. cinerea* plates. Plates in four replicates were used for each treatment, and the inoculated plates were incubated in the dark at 27°C. Growth inhibition was calculated as the percentage of inhibition of radial growth relative to the control.

Statistical Analysis

The results reported in this chapter are the averages of at least three replicates. Significant variables were calculated, subjecting results to a linear regression, using SPSS statistical program version 11.5 at a confidence level superior to 95% ($P < 0.05$). Difference between means was evaluated by Tukey's post-hoc test. The same SPSS software was used to calculate correlation coefficients (R) to determine the existence of any relationship between antioxidant power and phenols concentration.

For statistical analysis all the percent data were transformed into arcsin values.

Results and Discussion

The influence of starting material (marc or stalks) on final phenols yield (evaluated as GAE by direct absorbance reading at 280nm) was not statistically significant (Figure 4a). However, it must be said that ethanol extraction from grape stalks gave a crude extract that was partly ethanol and partly water soluble, that is to say two different extracts were obtained. Considering separately the two stalks extracts, marc gave always statistically higher GAE recovery. On the contrary, phenols content of extracts was higher for stalks extracts (Figure 4b). This could be due to the fact that stalks are a lignocellulosic material, whose main components lignin, cellulose and hemicelluloses can be separated only after strong acid and alkaline hydrolyses [92].

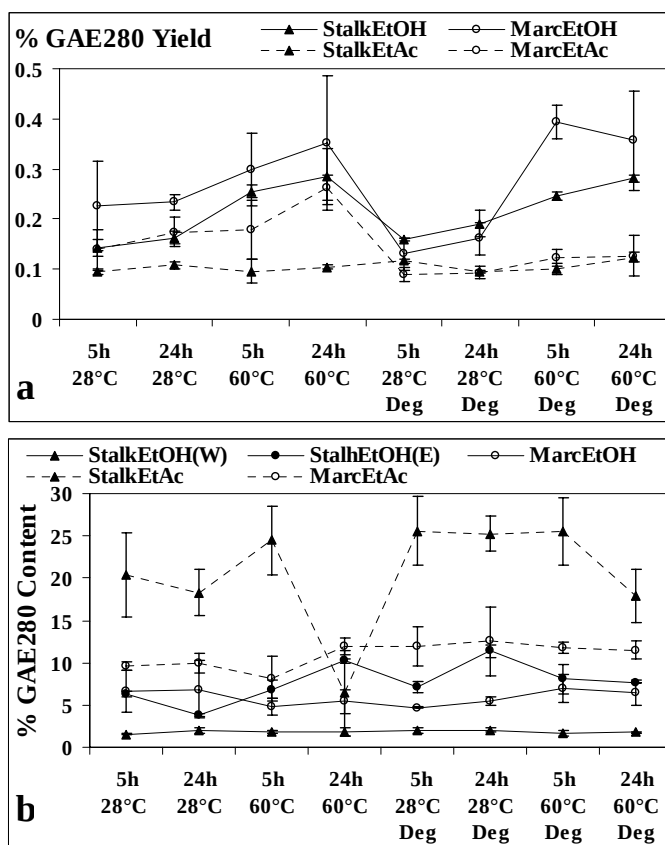


Figure 4. Phenols yield (a) and content (b) of extracts obtained with ethanol (EtOH) and ethylacetate (EtAc) from both grape marc and stalks (Deg: degreased sample; E: ethanol soluble extract; W: water soluble extract). Error bars indicate $\pm$ s.d.

The influence of the other investigated process parameters was then evaluated for marc and stalks separately.

Degreasing did not seem a useful pre-treatment because it reduced GAE yield and improved only slightly the phenols content of stalks-extracts.

Type of solvent was always highly significant. Extract purity was higher by using ethylacetate, particularly with stalks and, in fact, it is reported that the use of methanol, ethanol, acetone and their mixtures with water in different proportions generally yields a significant co-extraction of concomitant substances, which makes the procedure of extract purification more difficult and decreases the yield of target antioxidants [60], while ethylacetate exhibits significant selectivity in respect of natural products. On the other hand ethanol allowed for higher yields.

There was no significant difference between 5 and 24h, but this was not in agreement with some literature results. It was found out that in water-extracts made of grape the yield of polyphenols gently increased with the time, while in the case of alcohol-extracts it strongly increased with the longer time of extraction [44]. Other authors [60] reported that the kinetics curves of proanthocyanidins yield were of parabolic shape with the initial part being linear (up to 8h), whereas their second parts showed a slower increase and an asymptotic ending. In most of the cited references the effect of time was not an investigated factor, with a length of extraction varying from less than 1 h to 48 h.

Temperature was strongly influent on GAE yields for both marc and stalks, but not on extract purity, probably because temperature increase favoured extraction by increasing solubility and diffusion coefficient of any compounds, not only of antioxidants.

The AAI ranged from 40 to 80 with no influence of solvent, time, temperature and degreasing, while stalks extracts showed a slightly higher power than marc ones. Correlation between AAI and GAE concentration was positive and significant ($P < 0.01$), but weak (Pearson correlation coefficient of 0.42). Positive and variable coefficients (0.23-0.96) were reported also by other authors [37, 58]. In general, even using other assays for the antioxidant power, it is observed that the protection linearly increases with the antioxidants concentration up to a certain value, above which the increase is slower or absent. Furthermore, the degree of correlation depends on the class of compounds and is generally higher for total polyphenols than for anthocyanins, flavonoids or flavonols [26, 27, 55, 69]. The used β -carotene test is simple and can give a screening evaluation of the antioxidant power, but it gives poorly reproducible results (due to variations in β -carotene bleaching reaction), it is not specific (being subject to interference from oxidation and reducing agents in crude extracts), and linoleic acid is not representative of typical food lipids.

GAE yield and content data reported in Figure 4 could have been underestimated for two reasons. First of all samples could not be concentrated to a powder, but to a viscous and dense paste (probably due to the presence of sugars and fats); secondly, after addition of petroleum ether to marc extracts a solid precipitate was not separated.

On the basis of these initial results, the extraction procedure was tried to be improved focusing on employment of grape marc. The step of precipitation by petroleum ether was substituted by freeze-drying. Analysis of extracts before and after freeze-drying assured that the operation did not reduce antioxidant activity of extracts.

The particle size of 2mm and the solvent/sample ratio were not varied on the basis of the literature data already commented.

The next experiments were then aimed to verify whether an intermediate temperature between 28°C and 60°C could give the same recovery yield as 60°C (or even higher in case a certain degree of thermal degradation occurred at 60°C) in order to reduce the energy cost of the process; and to demonstrate if the equivalence of yield at 5 and 24 h was due either to the

achieving of a plateau at 5 h, or to any antioxidants degradation taking place after an intermediate maximum.

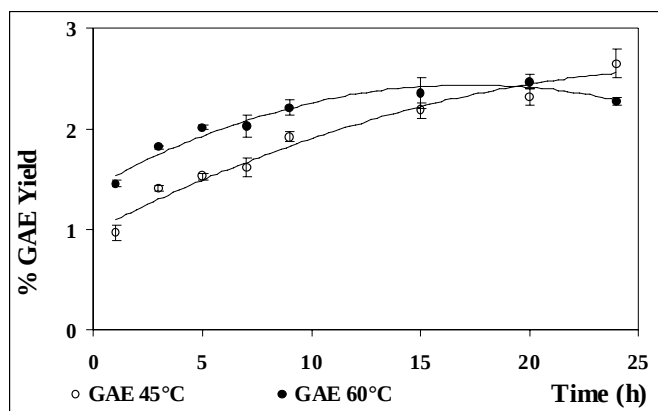


Figure 5. Phenols yield for trials at different temperatures and times (error bars indicate $\pm$ s.d.).

Statistical analysis of results (Figure 5) indicated that both time and temperature highly influenced antioxidants yields with higher yields at 60°C. Tukey's post-hoc test confirmed that yield increased with length of maceration but at 60°C there seemed to be a reduction beyond 20 h due to thermal degradation, or phenols polymerization which may influence analytical quantification [63]. Effect of temperature cannot be generalised since it strongly depends on typology of compounds. For example, it has been reported [15] a maximum of 30-35°C for extraction of anthocyanins from ribes with ethanol 85%; while it has been indicated 20°C and 0°C for the highest yields of ethanolic extraction of carnosic acid, and of both ursolic acid and oleanolic acid, respectively, from Balm leaves [32]. On the other hand, it was shown [45] that drying red grape pomace peels at 60°C did not significantly affect the stability of polyphenols and antioxidant activity, and, indeed, it was reported an increase in the antioxidant capacity of grape extract by means of a simple thermal treatment at 60°C, due to phenols polymerization [39, 65].

Time was a significant variable, particularly at 45°C, while at 60°C yields after 5 and 24 h were different but means fell into two adjacent homogenous groups (mean discrimination through Tukey's test), confirming the previous results. Intermediate and higher values were reached in agreement with other literature works [60] and many time-temperature combinations gave actually the same results. From a recovery point of view it would be more convenient to work at lower temperature for longer time. However, considering extraction rates of Figure 5 and bearing in mind an industrial application of the process, it could be more convenient and energetically less expensive to work at higher temperature for shorter times (possibly < 8 h). That's why extraction at 60°C for 5h was selected, even though leading to lower yields. An accurate economical evaluation of the incidence of energy cost of the extraction stage on the overall production cost per unit mass of final extract is required to confirm this choice.

In order to further increase the recovery, we moved onto investigating the influence of addition of water to ethanol, since mixtures of alcohols and water have revealed to be more efficient in extracting phenolic constituents than the corresponding mono-component solvent

system [61, 106]. Regarding grape and wine-making wastes, influence of water content of alcohols has been studied only for extraction from seeds [3, 106]. In fact, ethanol, a polar solvent, effectively extracts flavonoids and their glycosides, catecols and tannins from raw plant materials [12], but solubility of these compounds can be enhanced using a mixed solvent over a limited compositional range [15].

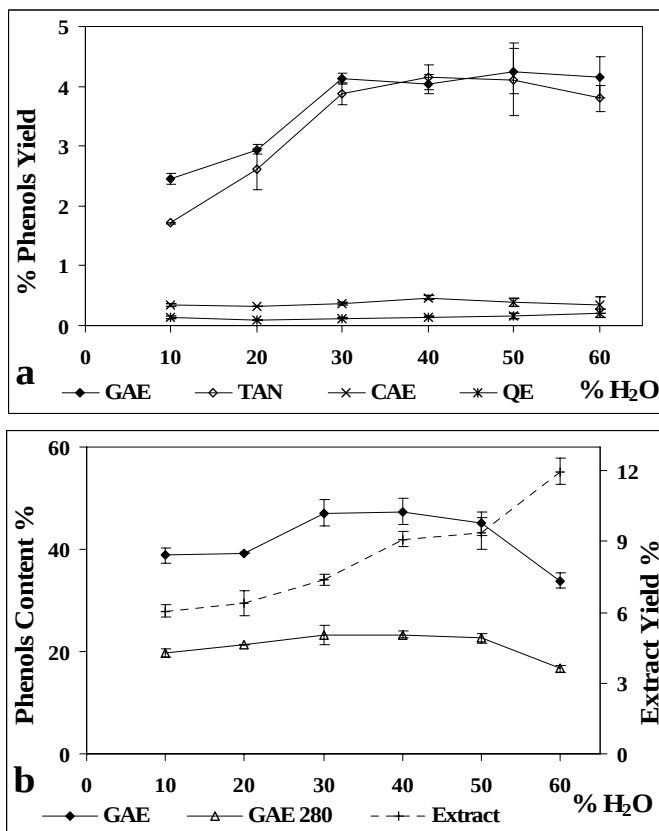


Figure 6. Influence of water content of ethanol on phenols yield (a), freeze-dried extract yield and phenols content (b) (error bars indicate $\pm$ s.d.).

Phenols yields obtained at increasing water content of ethanol are shown in Figure 6a. In these trials the phenolic composition of the extracts were better characterised evaluating also the content of tannins, cinnamic acids, flavonols, and anthocyanins. Trend for the latter compounds was not shown because yields were always lower than 0.012%, due to the levels of anthocyanins in grapes and to the fact that for red wines, they are mainly extracted during fermentation and vinification processes. Total phenols were evaluated by both the Folin-Ciocalteu method and direct absorbance reading at 280nm. Figure 6b shows clearly that yields of total phenols based on GAE-280 were lower but highly correlated to those based on GAE (Pearson's correlation coefficient +0.967, Sig. 0.000). The different results are due to the different principle of the two analytical methods: reaction with an oxidising reagent in the Folin-Ciocalteu analysis, absorption of the aromatic ring in direct reading at 280nm. This

explains also why yields obtained in the second set of experiment (Figure 5) were higher than those obtained in the first one (Figure 4).

Increase of water content of ethanol was statistically influent in improving extraction yield for GAE, GAE-280, tannins, and total extract, but not for cinnamic acids and flavonols. Tukey's post-hoc test confirmed that phenols yield was improved increasing the water percentage of ethanol from 10 to 30%, and, then, it did not significantly change for water content between 30 and 60%, while total extract yield kept on increasing with water content. Similar trends were reported by other authors. It was reported [106] that phenol content (as GAE) of ethanol extracts from grape seed powder increased increasing water in the mixture from 0 to 30%, kept constant for 30-40-50%, and decreased for higher percentage. In another study [15] it was obtained that extraction of anthocyanins from black currants using aqueous ethanol increased with ethanol concentration up to a maximum at about 60% and then decreased with further increase in solvent concentration. In the same work it was suggested a different optimum ethanol content for the extraction of each group of phenols.

On the other hand, according to the fact the total extract yield kept on increasing with water content, concentration of phenolic constituents in the extracts increased for water content from 10 to 30%, and decreased for water content above 50% (Figure 6b), so a value of 40% was retained as the optimal one.

It must be pointed out that freeze-dried extracts had to be dissolved in the same mixture ethanol/water used for their extraction, in order to get a complete solubilization without heating assistance. Solubilization problems should be taken in consideration for final employment of the extracts in food systems. For example, flavonoids modification by lipase-catalysed esterification has been reported to improve their solubility in lipid-base media [28, 40], and in natural antioxidants commercially exploited a proper medium, such as maltodextrine and propylene glycol, is incorporated to the same purpose. Statistical analysis (Students' t-test for paired samples; $\alpha = 0.01$) confirmed freeze-drying did not lead to reduction in phenols content, except for the cinnamic acids which seemed to get lost through freeze-drying. Actually, they are very sensitive to oxidation processes due both to enzymes (such as tyrosinase which is easily co-extracted from marc) and oxygen. Liquid extracts were stored in closed flasks but not under nitrogen, under refrigeration (oxygen solubility in water is increased at low temperature) and for a variable period of time before freeze-drying, and this may have brought to their rapid degradation.

Antioxidant power of extracts was this time evaluated by the ABST test due to the limits encountered with the β -carotene assay, and since the ABTS assay is reported as one of the best method for antioxidant activity measurement [67]. Results (Figure 7a) confirmed the correlation between antioxidant power and phenols concentration, and showed also that there was no difference between the various extracts, water content seemed only to influence the amount of phenols recovered but not their composition. To compare our results with other similar literature works, % inhibition was transformed into TEAC values (Figure 7b). TEAC value was concentration-dependent as observed in other works [16, 26, 79, 101], because in the considered range antioxidant activity linearly increased with concentration up to a certain value, above which the increase was lower or absent, while a linear Trolox® calibration curve was used for TEAC calculation. Values of TEAC were comparable to those of many other phenolic compounds and vegetable extracts [6, 70, 101, 107]. Only a paper reported very high TEAC data (from 10 to 140) for grape marc extracts [29].

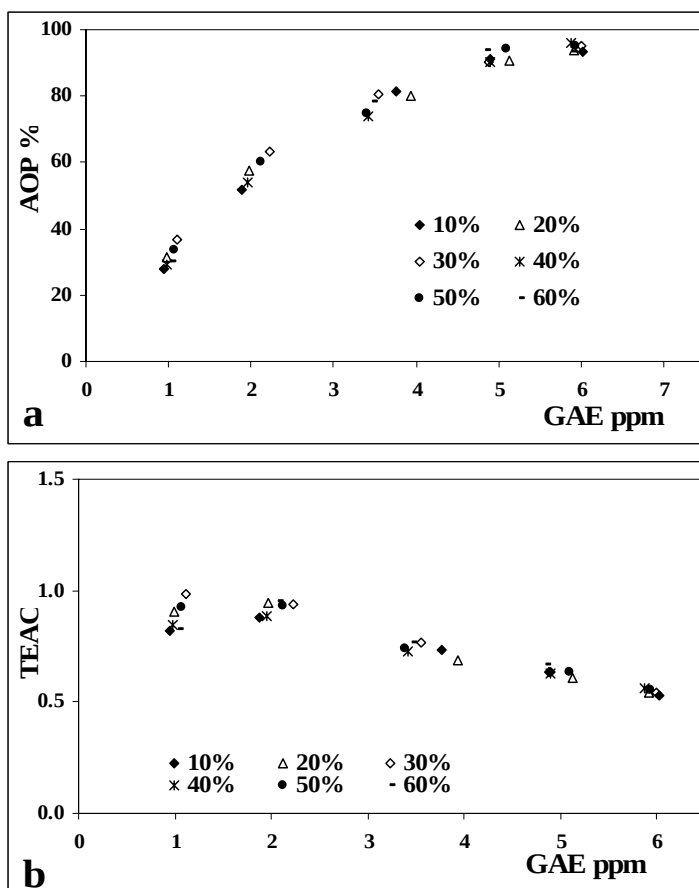


Figure 7. Antioxidant power (a) and TEAC values of extracts (b) as a function of phenols content.

Recovery trials at the selected conditions of 60°C, 5h, ethanol with 40% water, were performed on different types of grape marc. For the same grape variety, a different vintage can greatly change the phenols yield without influencing the phenols content of the extract, due to the influence of weather and season on grape ripening and composition: this is the case of data indicated as 2004 and 2005 in Figure 8. Employment of different grape varieties inevitably leads to both different yield and phenols content: undistilled samples of Figure 8 were obtained from marc coming from a mixture of white and black grape. Finally, distillation seemed not to reduce the phenols recovery and extract purity. According to other authors [17, 60, 61] results confirmed the possibility of extracting antioxidants also from distilled grape marc, that should be even a cheaper by-products than marc collected after devatting.

Knowledge of phenols extraction kinetics should provide a useful tool for scaling-up and process design. Data of Figure 5 were elaborated according to the quite simple model reported by [32]. The authors explained the kinetic plots of antioxidants extraction from Balm leaves by the presence of two extraction stages: an initial fast step corresponding to recovery of solutes from the superficial sites of the raw material, and a second lower step corresponding to molecular diffusion of solutes from the internal sites through the porous

medium. For both the steps, application of the steady-state model leads to the first-order rate equation:

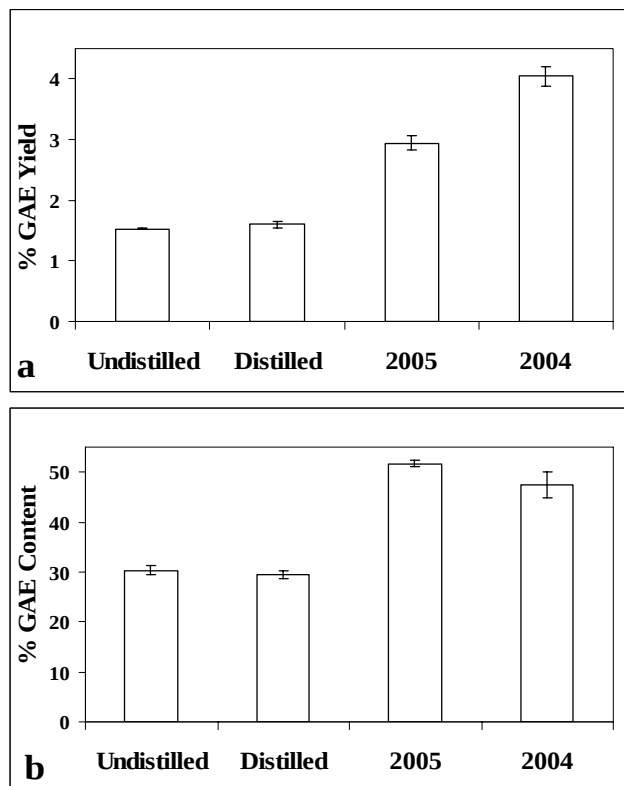


Figure 8. Phenols yield (a) and phenols content (b) of extracts obtained from Barbera grape marc of different vintages (2004 and 2005), and from grape marc other than Barbera before and after distillation (undistilled and distilled) (error bars indicate $\pm$ s.d.).

$$\ln\left(\frac{c_{\infty}}{c_{\infty} - c}\right) = k_{obs} \cdot t$$

where c is the concentration of the extracted constituent in the solution at time t , c_{∞} is its concentration at equilibrium ($t = \infty$), and k_{obs} is the overall rate constant (s^{-1}). The three rate governing steps of the process are: surface-controlled infusion, diffusion of the soluble constituents through the solid with a diffusion coefficient, and diffusion of the constituents through the Nerst layer with another diffusion coefficient. Considering the second step alone is rate determining, the k_{obs} takes into account the diffusion coefficient, the partition coefficient of the extracted constituents between the solvent and the solid, the total surface area, the volume of solvent and the size and geometry of solid particles. Considering the equilibrium concentration as that at 24 h for GAE extraction at 45°C, and that at 20 h before the apparent reduction for GAE extraction at 60°C of Figure 5, the second low step previously described (the fitting equations do not origin from zero) was able to describe our experimental results (Figure 9a), with an higher accuracy (smaller standard deviations) for the

short extraction time range previously selected. Extraction rate for time <5h was then investigated, varying also the stirring rate (by using the rotary shaker or a magnetic stirrer). Experimental data obtained by both the stirring modalities could be described accurately by the use of the characteristic function in the general case of a polydispersed anisotropic solid [84]:

$$C_l = A - B \exp(-Ht)$$

where C_l is the liquid phase concentration. The equation is expression of a first order kinetics model. Values of equation parameters reported in Figure 9b were obtained by non linear regression (SPSS software). The increase in stirring rate almost duplicated the phenol concentration. Extract quality was monitored through estimation of the tannins percentage by the PVPP method. Percentage of tannins of the extracted phenols did not significantly change with extraction time (Figure 9b), such as the AOP which for all the samples showed the same trend as a function of GAE concentration.

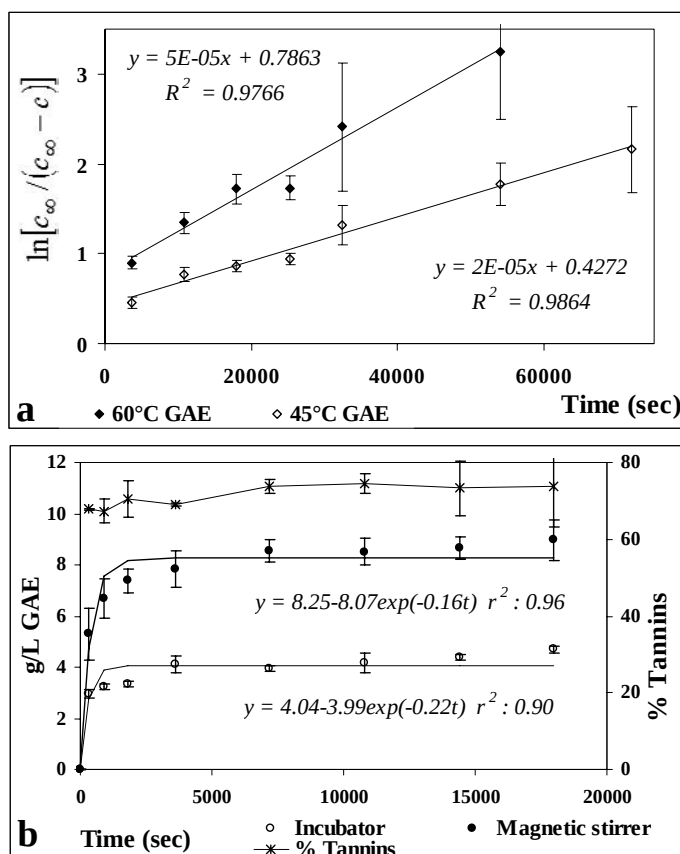


Figure 9. First order plot for the slow stage of phenols extraction at 45°C and 60°C (a), and extraction kinetics curves at different stirring modalities (b), with composition of phenols in terms of tannins percentage over time (error bars indicate $\pm$ s.d.).

Table 1. Comparison of different literature works on phenols extraction from grape and grape by-products.

Raw Material	Analysed compounds	Phenols Yield (%)	Phenols content of Extract (%)	References
Red Grape Marc	GAE	0.94-2.65	33.8-47.4	[93]
Red Grape Stalks	GAE	0.33	22.34	[90]
Red Grape Seeds	Catechins	0.86-1.56	43-54	[37]
Red Grape Seeds	Catechins	2.5	46	[36]
White Grape Seeds	Catechins	0.5	47	[60]
Fresh Grape seeds	GAE	10.8	66.8	[11]
Fresh Grape seeds	Catechins	0.078		[56]
Grape Seeds	Tannins		0.53	[1]
Fresh Red Grape Skins Fresh Grapes	GAE	0.25 0.43-0.51		[73]
Red Grape Marc	HPLC	0.11	0.011	[14]
Red Grape Marc	GAE	0.59	0.14	[53]
Seeds from Marc		2.4	0.28	
Skins from Marc		0.37	0.11	
Grape Marc	GAE	0.035-1.36		[44]
Grape marc	Flavan-3-ols	0.06		[29]
Distilled marc		0.08-0.14		
Grape seeds		0.15		
Distilled seeds		0.15-0.18		
Distilled Grape Marc	GAE	0.22	18.3	[17]
Grape seeds from marc	Epicatechin	0.08		[3]
Distilled red grape marc	GAE	0.16	1.07	[62]
Distilled red grape marc	GAE	0.25		[61]
Grape marc seeds	GAE	2.8-4		[106]

From comparison of literature works on phenols recovery from grape, phenols content of our extracts were very high and comparable to those obtained from only grape seeds, the part of the fruit richest in phenols (average tannin content of 3-6% on fresh weight and 4-11% on d.w.) (Table 1). It should also be pointed out that many of the cited references in Table 1 reported the application of more complicated recovery procedures (multiple-solvent-multiple step extractions). Phenols concentration is always around 50%, this is because alcoholic and aqueous extracts (solvents not selective for phenols) from fruits processing by-products contain inevitably sugars and polysaccharides. From a commercial point of view, a higher purity would give a higher value to the extract. However, purification by C_{18} resins or other columns to eliminate sugars, non volatile acids and amino acids [85] is an expensive step, inevitably separates free from bound polyphenolics, or different phenols classes (mixing of which may bring to antioxidant synergistic effect) [79], while, depending on the extracts application (dietary supplies, antioxidants into food systems) sugars removal might be not necessary. Employment of colloidal gas aphrons as an alternative simpler and cheaper purification system has been investigated [91]. Furthermore, there are still many uncertainties about polyphenols effective bioavailability and metabolism, i.e. *in vitro* positive effects have been shown for concentrations that are not reached *in vivo*, and even though much has been learned about possible mechanisms of actions, it is largely unknown whether they can reach their multiple intended sites of action and whether they are better absorbed as aglycones or glycosides [103].

Food Applications of the Extracts

Addition of marc extracts to vegetable oil showed a prooxidant effect, since the peroxide value was higher than in the control (Figure 9a). It was visually observed that extracts did not well solubilize into the oil but formed a reddish layer on the glass at the interface oil/air. This is not in agreement with other works which found a certain (not always high) protection of oil oxidation by different natural extracts [9, 13, 96]. However these works did not report a detailed description of the solubilization procedure, and it has been reported about the problems of solubility of green tea extracts into edible oils [54].

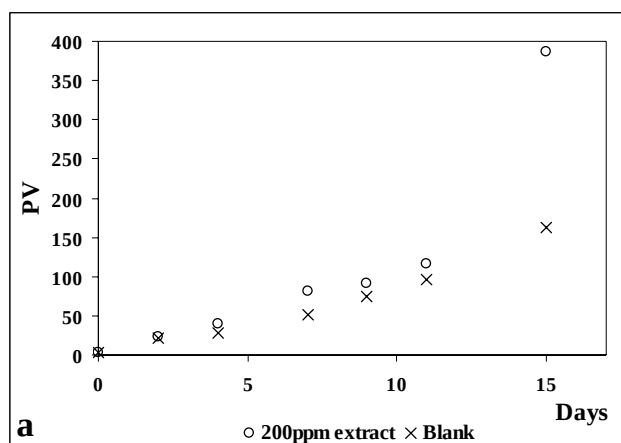


Figure 10. Continued on next page.

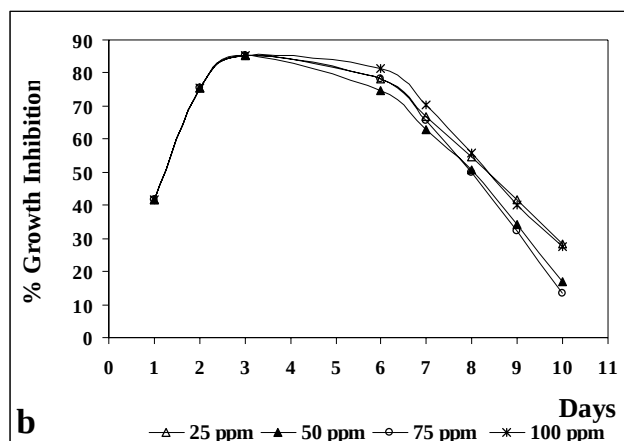


Figure 10. Application of marc extracts to inhibit oil oxidation (a) or to inhibit growth of moulds isolated from diseased strawberries (b).

Plant phenolics have been shown to be active against fungi. These compounds could then be exploited for developing improved and potentially safer technologies for postharvest disease control of fruits and vegetables [21, 46, 50, 71]. The shelf-life of strawberry is very short because of its perishability and susceptibility to rot-causing pathogens. During storage and shipping of strawberries, decay losses are mainly caused by *Botrytis cinerea* and *Rhizopus stolonifer*. Incorporation of different concentrations of our extracts into agar plates slowed down the growth of *B. cinerea* (Figure 10b). Complete inhibition, however, was not achieved at the concentrations tested, indicating that the phenols extracts are fungistatic rather than fungicidal. Their employment in combination with adequate packaging and refrigeration could greatly extend strawberry shelf-life.

Conclusion

The interest for production of natural antioxidants to be used instead of synthetic ones in food and pharmaceutical sectors has been greatly increasing in these last years.

Phenolic compounds represent the majority of natural antioxidants, and they can be potentially recovered from many sources since they are ubiquitous in plants. Their extraction from agricultural and food by-products is a great opportunity which would allow at the same time valorisation of wastes and reduction of production costs.

Recovery of phenols from natural sources involves many problematic aspects: choice of an adequate source (in terms of availability, cost, difference in phenolic content with variety and season); selection of the optimal recovery procedure (in terms of yield, simplicity, industrial application, cost); chemical analysis of extracts (for optimisation purposes a fast colorimetric method is preferable than a chromatographic one); evaluation of the antioxidant power (preferably by different assay methods).

Experimental results from a research carried out for recovery of phenolic compounds from wine-making by-products (grape marc and stalks) showed how it was possible to get a better insight into optimisation of the process, investigating some variables which were selected on the basis of the available literature about the same subject. The simple procedure

chosen (one solvent-one step extraction) gave results comparable to other literature results obtained with similar, longer or more complicated systems, even though it could be further improved by means of ultrasound or microwave assistance.

Knowledge of extraction kinetics is necessary in order to minimise production costs and to provide a useful tool for scaling-up and process design.

Application of the extracts into real food systems should always be verified since antioxidant mechanism can be quite different than in the model systems used in the screening fast methods commonly employed for evaluation of antioxidant power.

The optimal storage conditions and shelf-life of extracts as a function of antioxidant activity has to be investigated and established.

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Chapter 4

MATHEMATICAL MODELING OF FOOD DRYING PROCESS

***Stefano Curcio^{*}, Maria Aversa, Vincenza Calabrò
and Gabriele Iorio***

Department of Chemical Engineering and Materials,
Ponte P. Bucci – cubo 45/a, University of Calabria – Rende (CS) - ITALY

Abstract

Mathematical modeling represents a very important and effective tool for a proper design and control of industrial processes. A model reliably predicting a particular transformation process can, in fact, be used to investigate how the outputs may change with time under the influence of changes of the external disturbances and manipulated variables. In this way, it is possible to optimize the process, thus improving the quality and the safety of the final product. A mathematical model is, generally, based on a relationship, expressed in form of an equation (or a system of equations), whose solution yields the dynamic or static behavior of the process under examination. Both finite element method (FEM) and finite difference (FD) modeling have been utilized in food engineering research. A detailed analysis of the literature in the last 15 years shows that FEM applied to heat transfer dominates the publications, followed by diffusion calculations and drying process simulations. It is to be remarked, however, that a widespread use of mathematical modeling in food engineering is far from being well assessed.

The main aim of the present chapter is to analyze the transport phenomena involved in food drying process, performed in a convective drier. The formulation of two different theoretical models will be presented, focusing the attention on the differences that may be obtained if a simplified or a more complete analysis of the same transport problem is adopted. Both the models describe the simultaneous transfer of heat and moisture occurring during drying process. Actually, the first approach is much simpler, even though it could be considered a very important advance with respect to the theoretical analyses that are currently available in the literature. On developing the “simple” model, only food domain has been taken into consideration; moreover, heat and mass transfers occurring at the food surface exposed to the drying air have been estimated on the basis of a set of semi-empirical correlations available in the literature. The second model, instead, takes into account also the behavior of the drying air flowing, in turbulent conditions, about the food sample. This

^{*} E-mail address: stefano.curcio@unical.it. Tel. +39 0984 496711; Fax: +39 0984 496655.(Corresponding author)

approach is, therefore, more general since it describes the simultaneous transfer of momentum (for air only), of heat and mass (for both air and food) occurring in a convective drier and does not need the specification of any heat and mass transfer coefficient at the food-air interface that, indeed, is one of the results of the proposed model.

Both the models receive - as inputs - only the initial conditions, the geometrical characteristics of both food and drying chamber and the relationships expressing physical and transport properties of food and air in terms of the local values of temperature and moisture content. The resulting system of non-linear, unsteady-state partial differential equations has been solved by means of the Finite Elements Method. The comparison between two possible different approaches may suggest if a significant increase of computation effort is actually required or, instead, if the utilization of a much simpler and faster method is capable of giving a proper description of the process under consideration. The main objective of the present work is to show how an accurate transport model can be used to determine the influence of operating conditions on drying process. In this way, it might be possible to minimize expensive pilot test-runs and have good indications on the characteristics and the quality of dried products.

Introduction

General Considerations on Drying Process

Drying, or dehydration, is one of the most common unit operation utilized for food preservation. The words drying and dehydration are often reported as synonyms even though it is more appropriate to define a food as dehydrated when its water content is rather low, typically less than 2.5% (Barbosa-Cànovas and Vega-Mercado, 1996). The decrease of water content in food allows reducing both microbial spoilage and deterioration reactions since water is essential for the metabolism of several bacteria and microorganisms. Moreover, food drying can reduce packaging, handling, storage and transport costs because a decrease of food weight and, in most cases, also of its volume is achieved. Several different techniques are used to perform water removal. Among these, freeze-drying, osmotic drying, vacuum drying, microwaves or radio-frequency drying are very well known and are adopted in several industrial applications. Nevertheless, drying by dry and hot air flowing about food samples is, definitely, the most common industrial method to promote water transfer from food, thus reducing its moisture content. On analyzing drying process, it is necessary to characterize the mechanisms determining the water transport within, but also, outside the food. Actually, water transport may be due to a combination of different phenomena: i.e. inner diffusion of water due to concentration gradients, diffusion of water, as a vapor, in the pores filled with air, capillary forces, convective flow determined by pressure differences and flow of water due to vaporization/condensation.

A proper analysis of drying process is usually performed monitoring the variation of food weight with respect to time. The collected experimental data allow calculating the time evolution of food moisture content, X , defined as the ratio (on a mass basis) between the actual amount of water in the food and the amount of dry solids. It is, however, more significant to introduce another variable, i.e. the so called free moisture content, X_f , defined as the difference between X and the moisture content that can be measured when equilibrium conditions are attained, X_{eq} . A drying curve, shown in a typical case in Fig. 1, is obtained plotting free moisture content versus time.

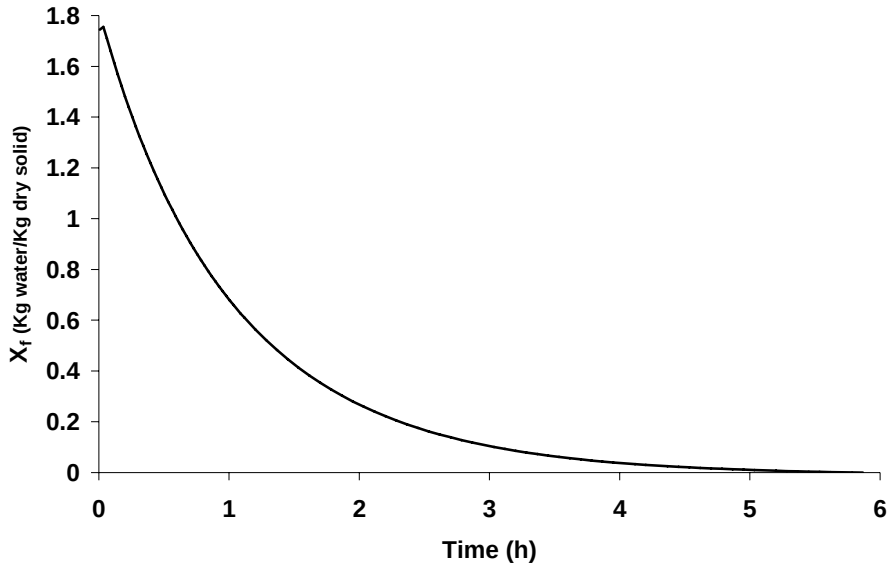


Figure 1. Drying curve in a typical situation.

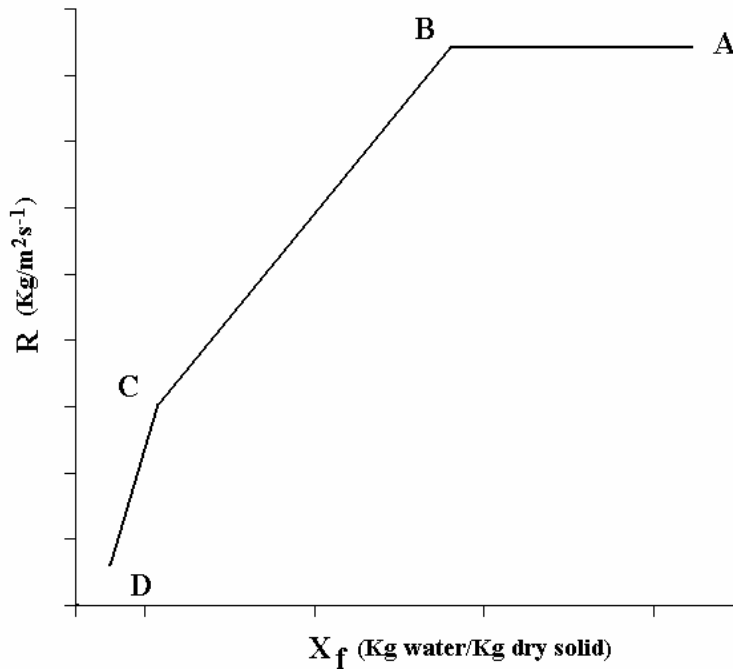


Figure 2. Relationship between drying rate and free moisture content in a typical situation.

The drying rate, R , is proportional to the time derivative of X_f ; therefore, the slopes of the drying curve, evaluated for each point, may be used either to estimate the time evolution of drying rate or to determine, as shown in Fig. 2 from a qualitative point of view, the relationship existing between drying rate and free moisture content.

An examination of the above figure puts in evidence that drying usually takes place in different stages, each characterized by a different rate. The initial stage, where drying rate does not change with respect to X_f (line A-B), is known as the constant drying rate period. During this phase, vaporization occurs at the product surface and only unbound water, i.e. the water characterized by unity activity coefficient, is removed from the product. The transport phenomena mostly involved in this stage are the mass transfer of water, as a vapor, from the food surface into a boundary layer developing in the drying air and the heat transfer in the material. The rate at which water is transported from the inner parts of the food is very fast and is capable to compensate the amount of water evaporating at the surface that, therefore, maintains saturation conditions. The temperature of food surface is approximately equal to the wet bulb temperature.

The second stage, known as the falling rate period, starts when free water is no longer available at the surface; water activity on the surface tends to decrease and assumes values lower than unity. The falling rate period may be subdivided in two following stages, recognizable by different slopes in R vs. X_f curve. The first period takes place until food surface is entirely dry (line B-C). The second one, instead, is characterized by a displacement of evaporation front from the surface to food internal regions (line C-D); water vapor has to diffuse through a thicker and thicker layer of already dried material before reaching the surface where it mixes with the air flowing about the sample. During falling rate period, the amount of water removed from the food may be rather small and, consequently, the time necessary to complete this stage is, generally, long. This is mainly due to the fact that drying rate is controlled by diffusion of water toward the surface. Actually, the transport of water within the food structure is a rather complicated phenomenon that can be explained with reference to several mechanisms that include the diffusion of liquid promoted by concentration gradients, the diffusion of water, as a vapor, due to partial vapor pressure differences, the transport of liquid water caused by either capillary or gravity forces, the surface diffusion. In spite of the complexity of the above-described phenomena, a simple diffusion equation based on Fick's law has been widely used in the literature to describe the dependence of food moisture content upon time and position. Nevertheless, it is suggested to make use of an effective diffusion coefficient (D_{eff}), a parameter estimated from the experimental data collected during drying process that accounts for the interactions existing between the water to be transported and the food structure.

Convective Food Drying

When dry and warm air flows about a moist and cold food sample, a simultaneous transfer of both heat and water occurs. In particular, heat is transferred from air to the material; water is transported from the food core, then, to its surface and, eventually, to air. The rates of heat and mass transfer depend on both temperature and concentration differences, but also on the air velocity field that strongly affects the transfer rate and, therefore, has to be properly evaluated. Typical values of air temperature range between 35°C and 80°C, air relative humidity varies between 10% and 70%, while air normally flows at a velocity ranging from 0.5 to 5 m/sec, reaching - in some cases - the value of 10 m/sec. The main aims of convective drying are a decrease of food water content and an increase of its temperature: both the above

effects improve food preservation since microbial spoilage is favored by low temperature and high moisture content.

Convective drying is definitely the most common method for food preservation, so several different approaches have been proposed to model this process (Wang & Sun, 2003; Datta 2007 Part I). The models available in the open literature may be subdivided in two categories: simplified and complex approaches. The latter are often regarded as too onerous and time consuming for practical purposes; the former, instead, are quite simple but are based either on simplification hypotheses, not applicable in several real cases, or on the utilization of empirical correlations, necessary to estimate - by means of a set of transport coefficients - the heat and water fluxes at food-air interface. In simplified models the utilization of the so-called *thin-layer equation* (Ertekin & Yaldiz, 2004; Doymaz 2004; Karathanos, 1999; Krokida, Karathanos, Maroulis & Marinou-Kouris, 2003) is quite common. It is based on the hypothesis that food moisture reduction is proportional to the instantaneous difference between the material moisture content (assumed uniform within the food) and the water concentration calculated under the assumption that equilibrium conditions with drying air do actually exist. A considerable simplification is, therefore, attained since the description of all the transport phenomena involved in drying process can be reduced to the solution of a single ordinary differential equation. The above-mentioned proportionality is expressed in terms of a constant, known as the drying constant, that is a function of several parameters such as the material moisture content, the size of product and its temperature distribution (assumed uniform), and the main characteristics of drying air, i.e. its humidity, temperature and velocity. Also other simplified models, based on a single equation but supported by fundamental considerations, were proposed; they actually model the water transport in food by means of Fick's diffusion equation and assuming that drying can be considered as an isothermal process (Hernández, Pavón, García, 2000; Simal, Femenia, Llull, Rossello, 2000). Nevertheless, a more rigorous approach should also take into account for the heat transfer in food (Wang, Brennan, 1995; Kalbasi, Mehraban, 2000; Migliori, Gabriele, de Cindio, Pollini, 2005) by means of Fourier's equation of conduction or, in a simpler way, assuming a uniform temperature profile in food, thus considering a macroscopic heat balance (Rovedo, Suarez, Viollaz, 1995). It should be observed, however, that all the above-mentioned models are based on the solution of a set of transport equations that are defined in terms of both fundamental transport properties, like the diffusion coefficient of water in food and the effective thermal conductivity of food, and physical parameters, like the heat capacity and the density of the material to be dried. Their values actually depend on food structure, on the local values of both temperature and moisture content and are very difficult to estimate due to the complex chemical and physical changes that take place during food drying. The importance of considering the variability of physical and transport properties with food temperature and moisture content was investigated by several authors (Datta, 2007 Part II, Panagiotou, Krokida, Maroulis, Saravacos, 2004, Lewicki, 2004). In particular, Datta described the different possible procedures that can be adopted for the evaluation of food properties; the author remarked the need to utilize a more rigorous methodology since every single complex phenomenon involved in food processing plays a crucial role and might strongly affect parameters estimation. Saravacos & Maroulis, 2001 confirmed this necessity, showing that huge differences are found in the literature as far as the estimation of the same property, such as the diffusion coefficient of water in the food and the food thermal conductivity, is concerned.

As it will be shown more in detail in the following section, the transport phenomena involved in food drying process are rather complex since they involve a simultaneous transfer of momentum, heat and mass. The governing equations form a set of un-steady, non-linear, partial differential equations that can be solved only by means of numerical procedures. Both finite difference (FD) and finite element (FEM) methods have been widely used for this purpose. It was reported that FEM is particularly suitable to perform investigations on domains characterized by irregular geometries, in presence of complex boundary conditions and for heterogeneous materials. Nevertheless, it is more complex and computationally expensive than FD (Wang & Sun, 2003). To solve drying balance equations, suitable boundary conditions, especially at food-air interface, are required. They could be either Neuman-type or Dirichlet-type; the former, however, gives better results than the latter (Markowski, 1997). Dirichlet-type boundary conditions are defined specifying at food-air interface both water concentration and food temperature. Neuman-type boundary conditions are defined with reference to a set of heat and mass transfer coefficients that are estimated from the experimental data collected during drying process. Most of available literature data are expressed in terms of semi-empirical correlations and refer to the estimation of heat transfer coefficient (Saravacos, Maroulis, 2001); the Chilton-Colburn analogy is, however, usually adopted to estimate mass transfer coefficient once heat transfer coefficient has been determined (Bird, Stewart, Lightfoot, 1960). These correlations are parametric equations expressed in terms of characteristic dimensionless numbers. In particular, Nusselt number, Nu , is related to both Reynolds, Re , and Prandtl, Pr , numbers by a general equation like:

$$Nu = a Re^b Pr^c \quad (1)$$

in which a , b and c are model parameters.

In the case of quite common geometries (i.e. slabs, cylinders, spheres), the model parameters are very well known in a wide range of fluid-dynamic and process conditions. In other practical cases, experimental test-runs have been performed to estimate model parameters as a result of best fitting procedures. The available data, however, put in evidence that large variations do, actually, exist (Saravacos, Maroulis, 2001). This is to be ascribed to the fact that even small differences in fluid-dynamic conditions or in food characteristics cause relevant deviations in the estimated values of transfer coefficients. As a matter of fact, Kondjoyan and Boisson, 1997) and Verboven et al. (1997 and 2001) verified that minor errors in the estimation of transfer coefficients, can lead to huge variations in the calculated time evolutions of both food temperature and its moisture content, thus leading to an unfair design of drying equipments or to severe problems during food processing. In principle, it should be observed that a very good prevision model might fail if heat and mass transfer coefficients are estimated by means of unsuitable literature correlations. In spite of this real difficulty, many authors proposed transport models based on the utilization of semi-empirical literature correlations to evaluate heat and mass fluxes at the food-air interface (Pavón-Melendez, Hernández, Salgado, García, 2002; Karim & Hawlader, 2005; Aversa, Curcio, Calabrò, Iorio, 2007; Wang & Brennan 1995). To overcome the problems related to the utilization of a proper set of heat and mass transfer coefficients, it would be, however, advisable to formulate a more general drying model. This is to be based on the resolution of the fundamental transport equations (momentum, heat and mass) in both air and food domains, achieved by

the utilization of a proper set of boundary conditions at the food-air interfaces. In this way, no literature correlation is actually required and the model might fit for all possible food shapes and all the operating and fluid-dynamic conditions. Nevertheless, a so exhaustive analysis has been often regarded in the past years as too onerous in terms of computational effort and calculation time.

In the following, two different approaches to the modeling of convective food drying process will be presented. The attention will be focused on the differences that can be obtained if either a simplified or a more complete analysis of the same transport problem is adopted. Both the models describe the simultaneous transfer of heat and moisture occurring during drying process. Actually, the first approach is much simpler, even though it could be considered a very important advance with respect to the theoretical analyses that are currently available in the literature. On developing the “simple” model, only food domain has been taken into consideration; moreover, heat and mass transfers occurring at the food surface exposed to the drying air have been calculated on the basis of semi-empirical correlations available in the literature.

The second model, instead, takes into account also the behavior of the drying air flowing, in turbulent conditions, about the food sample. This approach is, therefore, more general since it describes the simultaneous transfer of momentum (for air only), of heat and mass (for both air and food) occurring in a convective oven.

The main objective of the present chapter is to present a rather detailed analysis of the transport phenomena occurring during drying process in order to develop a proper transport model that can be used to simulate the behavior of real dryers. In particular, the comparison between two possible different approaches may suggest if a significant increase of computation effort is actually required or, instead, if the utilization of a much simpler and faster method is capable of giving a proper description of the process under consideration.

Theoretical

In the following, the main assumptions and the mathematical equations used to model the unsteady-state behavior of a convective drying oven will be shown for both the models that are to be developed.

It is supposed that drying air is continuously supplied to the oven inlet section and flows about the food, actually a vegetable, in the axial direction (y), parallel to its main dimension (Fig. 3). Heat and mass transfer resistance are assumed negligible across the net on which the vegetable is placed (Thorvaldsson, Janestad 1999; Viollaz, Rovedo, 2002). On the basis of the above hypothesis, the system under investigation can be considered as a classical symmetric one; a symmetry axis, in fact, may be individuated and only half of the original domains will be henceforth considered. Moreover, any possible variation occurring with reference to the spatial coordinate z is assumed not relevant for the present study. This allows analyzing a 2D geometry so that food sample can be considered as a slab and the oven as a rectangular chamber, characterized by a length of 25 cm and by a height of 10 cm. Food sample is placed 8 cm far from the oven inlet section and it is 6 cm long and 5 mm thick. Each dependent variable is expressed as a function of two spatial coordinates, x and y , and of time, t .

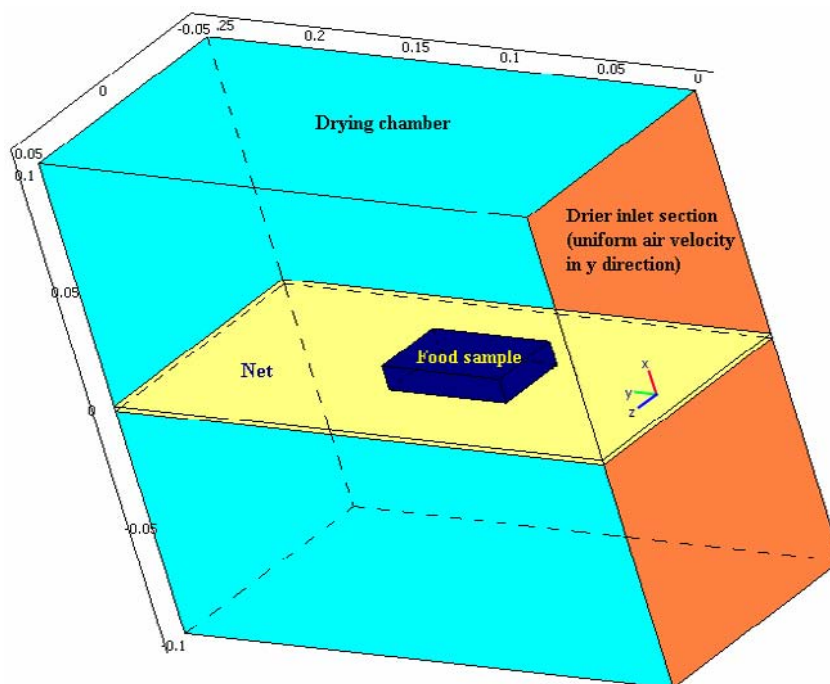


Figure 3. Schematic representation of the drying chamber under consideration.

Both the proposed models account for the variation of air and food physical properties, defined in terms of the local values of temperature and moisture content. As far as the food sample is concerned, a continuum approach has been chosen; it has been supposed, in fact, that the actual multiphase hygroscopic porous medium may be replaced by a fictitious continuum, any point of which has variables and parameters that are continuous functions of point spatial coordinates and of time. Convective contributions in the transport equations written for the food have been neglected, assuming weak inner evaporation. Also the transport of water vapor by diffusion within the dehydrated material toward the external food surface has not been considered since this mechanism is significant especially for highly porous media, whereas for the vegetables under consideration - typically characterized by void fraction lower than 0.3 (May & Perré, 2002) - can be neglected. Mass transfer in the product occurs, therefore, only by diffusion; heat transfer in the product occurs only by conduction. Shrinkage effects were assumed negligible in the range of average moisture content taken in consideration.

Simplified Approach

On the basis of the above discussion, water and heat transfers occurring during food drying process were modeled by the unsteady state mass and energy balances, respectively, whereas evaporation, occurring at air-food interfaces only, was considered by defining a proper set of boundary conditions expressed in terms of heat and mass transfer coefficients estimated by empirical correlations available in the literature (Perry & Green, 1984).

The energy balance in the solid, based on Fourier's law, leads to

$$\rho C_p \frac{\partial T}{\partial t} = \nabla \cdot (k_{eff} \nabla T) \quad (2)$$

where ρ is the food density, C_p is its heat capacity, T is the temperature, t is time and k_{eff} is the effective thermal conductivity of food.

The mass balance, based on Fick's law, leads to:

$$\frac{\partial C}{\partial t} = \nabla \cdot (D_{eff} \nabla C) \quad (3)$$

where C is water concentration in food and D_{eff} is the effective diffusion coefficient of water in food.

The subscript *eff* considers that food transport properties are evaluated as effective indexes, thus accounting for a possible combination of different transport mechanisms.

Supposing that the above material parameters and transport properties (ρ , C_p , k_{eff} , D_{eff}), in the most general case, depend on the local values of food moisture content and of temperature, Eqs. 2-3 form a system of unsteady, non-linear partial differential equations (PDEs). The expressions of ρ , C_p , k_{eff} , D_{eff} , derived by Ruiz-López, Córdova, Rodríguez-Jimenes, García-Alvarado (2004) in the case of carrot slices drying, have been used.

The initial conditions are straightforward since it has been assumed that before drying process actually begins ($t = 0$), food moisture content and its temperature have definite values, i.e. C_0 and T_0 , that are to be specified before performing each simulation.

The boundary conditions relative to eq. 2 apply to each external surface of the food sample, where no accumulation occurs; they actually state that the heat transported by convection from air to food is partially used to raise sample temperature by conduction and partially to allow free water evaporation:

$$h(T_{gb} - T_s) = -\underline{n} \cdot (-k_{eff} \nabla T) - \lambda N_s \quad (4)$$

where λ is the latent heat of vaporization for water, N_s is the diffusive flux of water at the food surface, h is the heat transfer coefficient, T_{gb} is the bulk temperature of air, T_s is the temperature at the food surface; $\underline{n}$ is a generic unity vector normal to the surface.

The boundary conditions relative to eq. 3, apply to each external surface of food sample, where no accumulation occurs; they express the balance between the diffusive flux of liquid water transported from the product core to the surface and the flux of vapor that leaves the food surface and is transferred to the drying air:

$$-\underline{n} \cdot (-D_{eff} \nabla C) = k_c (C_i - C_{gb}) \quad (5)$$

where k_c is the mass transfer coefficient, C_{gb} is the bulk concentration of water in air, C_i is water concentration evaluated in gaseous phase at the food/air interface.

An equilibrium relationship between the water concentration in the air and the water concentration, on the food surfaces actually exposed to the drying air, can be also formulated (Smith, Van Ness, Abbot, 1987):

$$\gamma_w x_w f_w = \hat{\phi}_w y_w p \quad (6)$$

The superscripts *v* and *l* (vapour and liquid, respectively) were omitted with the understanding that γ_w , the activity coefficient of water and f_w , the fugacity of water, refer to the liquid phase, $\hat{\phi}_w$, the fugacity coefficient of water, refers – instead - to the vapor phase; x_w and y_w are the molar fractions of water in food and in air, respectively, p is the pressure within the drying chamber. The fugacity of water can be expressed by:

$$f_w = \phi_w^{sat} P_w^{sat} \exp \left[\frac{V_w (p - P_w^{sat})}{RT} \right] \quad (7)$$

where P_w^{sat} is the vapor pressure of water, expressed in terms of the local values of temperature, and the exponential term is known as the Poynting factor.

If the quantity Φ_w is introduced:

$$\Phi_w = \frac{\hat{\phi}_w}{\phi_w^{sat}} \exp \left[- \frac{V_w (p - P_w^{sat})}{RT} \right] \quad (8)$$

The following relationship is obtained:

$$\gamma_w x_w P_w^{sat} = \Phi_w y_w p \quad (9)$$

At low pressures (up to at least 1 bar), vapor phase usually approximates ideal gases ($\hat{\phi}_w = \phi_w^{sat} = 1$) and the Poynting factor differs from unity by only a few parts per thousand; moreover, values of $\hat{\phi}_w$ and ϕ_w^{sat} differ significantly less from each other than from unity and their influence in eq. 8 tends to cancel. Thus, the assumption that $\Phi_w = 1$ introduces a little error for low-pressure vapor-liquid-equilibrium (VLE) and allows simplifying eq. 9 to:

$$\gamma_w x_w P_w^{sat} = y_w p \quad (10)$$

It should be observed that in hygroscopic materials, like most of the foods, the parameter γ_w accounts for the effects related to the amount of physically bound water so it is usually

expressed as a function of both food moisture content and of its temperature (Datta 2007 Part II, Ruiz-López, Córdova, Rodríguez-Jimenes, García-Alvarado, 2004). Once the activity coefficient is known for the particular food under examination, eq. 10 permits calculating the molar fraction of water in the vapor phase and, therefore, the value of C_i that appears at the right-hand side of the above eq. 5.

Eqs. 4, 5 and 10 are essential to properly describe the complex steps involved in drying process. Eq. 10, in fact, is expressed in terms of water activity coefficient γ_w that decreases as food moisture content decreases so that a unity value of γ_w means that only unbound (free) water actually evaporates. When $\gamma_w < 1$ also bound water is removed from the food sample. Water activity coefficient is a distinctive parameter of each product that, being characterized by its own structure, determines how strong the bonds between food structure and water are. Moreover, it should be observed that both the moisture content and the temperature on food external surfaces determine, through eq. 10, the value of food surface water concentration and then the time evolution of drying process. In particular, if on the food surface either moisture content or temperature are high enough to have $(C_i - C_{gb}) > 0$, then, on the basis of eq. 5, food drying starts immediately; whereas if their values are such to have $(C_i - C_{gb}) < 0$, then a preliminary humidification of food surface is observed. This, according to eq. 4, causes a steep food temperature raise owing to both the heat transfer by convection from air to food and the latent heat of condensation due to vapor condensing on food surface. The above phenomenon continues until food temperature is high enough to make $(C_i - C_{gb}) > 0$; at this point, according to eq. 5, drying begins and heat is transferred by convection from air to food whereas latent heat of vaporization is transported from food to water, thus allowing its evaporation (eq. 4).

As it will be specified in the following, heat and mass transfer coefficients have been estimated on the basis of the well-known semi-empirical correlations expressing the dependence of Nusselt number upon Reynolds and Prandtl numbers and of Sherwood number on Reynolds and Schmidt numbers, respectively (Perry & Green, 1984). It has been assumed that the Chilton-Colburn analogy holds.

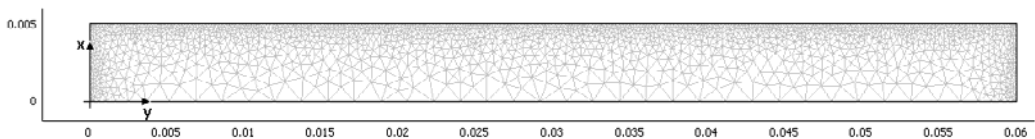


Figure 4. Discretization of food sample into triangular finite elements.

The above system of non-linear partial differential equations has been solved by the finite elements method developed by the commercial package Comsol Multiphysics 3.3, Comsol Sweden. The domain corresponding to food sample has been discretized into 3550 triangular finite elements (fig. 4) with a thicker mesh close to the boundaries actually exposed to the drying air. The total number of degrees of freedom was equal to about 15000. On a 1.4 GHz Pentium IV computer running under Linux, a typical drying process duration of 5 hours was simulated, on average, in about 5 minutes, using the time-dependent nonlinear direct solver already implemented in the Comsol package. It should be remarked that the proposed model

does not need any parameters adjustment, but only the specification of a set of input variables that can be varied within a specific range of physical significance to simulate food drying behavior at different operating conditions.

Complete Model

The development of the previous model is based on the utilization of a proper set of heat and mass transfer coefficients that are to be provided by literature correlation or by experimental test-runs. In both the above cases, there are certainly some problems. Literature data about heat and mass transfer coefficients do actually cover a limited number of possible situations as far as both the geometry and the operating conditions are concerned; experimental tests are time consuming and not general since they are performed with reference to a specific vegetable, dried using a rather restricted range of operating conditions. A better way to analyze food drying process might be the solution of the transport equations in both the domains (food and air) and the definition of a completely new set of boundary conditions at the food-air interfaces. In this way, heat and mass transfer coefficients can be, actually, considered as the final result of a complex calculation and not as the essential tool necessary to describe the transport phenomena involved in drying process.

Therefore, the simultaneous transport of momentum, heat and mass and momentum in the drying air is to be combined, to the previous PDEs 2-3 describing, on the basis of the same simplification hypotheses already formulated, heat and moisture transport within the food sample.

In the air, heat transfer occurs by convection and conduction whereas water transfer takes place by convection and diffusion. The convective contributions to heat and mass transfer have to be considered due to air circulation whose velocity field has to be determined solving the non-isothermal momentum transport equations in turbulent conditions, coupled to the continuity equation. Evaporation/condensation effects at the air-food interfaces are, also in this case, taken into account by a set of boundary conditions that, however, are completely different with respect to the previous simplified approach. As it will be described in the following, these boundary conditions express the continuity of temperatures, and of heat and mass fluxes at the food/air interfaces. Moreover, the same relationship between water concentration in air and food moisture content does exist and the thermodynamic equilibrium expressed by eq. 10 holds.

The non-isothermal turbulent flow of air within the drying chamber has been modeled by means of the well-known $k-\varepsilon$ model that is based on two additional semi-empirical transport equations for the variables k and ε , i.e. the turbulent kinetic energy and the turbulent energy dissipation rate, respectively.

The unsteady-state momentum balance coupled to the continuity equation written for the drying air lead to (Bird, Stewart, Lightfoot, 1960; Verboven et al. 1997; Verboven et al. 2001):

$$\frac{\partial \rho_a}{\partial t} + \nabla \cdot (\rho_a \underline{u}) = 0 \quad (11)$$

$$\rho_a \frac{\partial \underline{u}}{\partial t} + \rho_a \underline{u} \cdot \nabla \underline{u} = \nabla \cdot \left[-p \underline{I} + (\eta + \eta_t) (\nabla \underline{u} + (\nabla \underline{u})^T) - (2/3) (\nabla \cdot \underline{u}) \underline{I} \right] \quad (12)$$

$$\rho_a \frac{\partial k}{\partial t} + \rho_a \underline{u} \cdot \nabla k = \nabla \cdot \left[(\eta + \eta_t / \sigma_k) (\nabla k) \right] + \eta_t P(\underline{u}) - (2\rho_a k / 3) (\nabla \cdot \underline{u}) - \rho_a \varepsilon \quad (13)$$

$$\rho_a \frac{\partial \varepsilon}{\partial t} + \rho_a \underline{u} \cdot \nabla \varepsilon = \nabla \cdot \left[(\eta + \eta_t / \sigma_\varepsilon) (\nabla \varepsilon) \right] + (c_{1\varepsilon} \varepsilon / k) [\eta_t P(\underline{u}) - (2\rho_a k / 3) (\nabla \cdot \underline{u})] - c_{2\varepsilon} \rho_a \varepsilon^2 / k \quad (14)$$

where ρ_a is the air density, η is its viscosity, both expressed in terms of the local values of temperature and water content, p is the pressure within the drying chamber, $\underline{u}$ is the velocity vector. c_μ , σ_k , σ_ε , $c_{1\varepsilon}$ and $c_{2\varepsilon}$ are constants whose value depends on the particular k - ε turbulence model that is used; in the case of the present analysis, the standard k - ε model has been adopted (Verboven 2000). The term $P(\underline{u})$, finally, contains the contribution of the shear stresses:

$$P(\underline{u}) = \nabla \underline{u} : (\nabla \underline{u} + (\nabla \underline{u})^T) - (2/3) (\nabla \cdot \underline{u})^2 \quad (15)$$

The following definition for η_t , i.e. the turbulent viscosity, in Eqs. 12-14, holds:

$$\eta_t = \rho_a \cdot c_\mu k^2 / \varepsilon \quad (16)$$

The energy balance in the drying air, accounting for both convective and conductive contributions, leads to (Bird, Stewart, Lightfoot, 1960):

$$\rho_a C_{pa} \frac{\partial T_2}{\partial t} - \nabla \cdot (k_a \nabla T_2) + \rho_a C_{pa} \underline{u} \cdot \nabla T_2 = 0 \quad (17)$$

where T_2 is the temperature of air, C_{pa} is its specific heat and k_a its thermal conductivity.

The mass balance in the drying air, referred to the water and accounting for both convective and diffusive contributions, leads to (Bird, Stewart, Lightfoot, 1960):

$$\frac{\partial C_2}{\partial t} + \nabla \cdot (-D_a \nabla C_2) + \underline{u} \cdot \nabla C_2 = 0 \quad (18)$$

where C_2 is the water concentration in air and D_a is the diffusion coefficient of water in air.

Since physical and transport properties of both air and food are expressed in terms of the local values of temperature and moisture content, eqs. 7-18, together with eqs. 2-3 describing heat and moisture transport in the food, represent a system of unsteady, non-linear partial differential equations that can be solved only by means of a numerical method.

A set of proper initial conditions is necessary to perform the numerical simulations. The initial conditions are referred to both air and the food. In particular, water concentration, C_{20} , temperature, T_{20} , the pressure and the velocity field in the drying chamber, $p_0 = p_{\text{atm}}$ and $\underline{u} = \underline{0}$, have been fixed for air before drying process takes place, whereas the initial values of

moisture content, C_0 , and temperature, T_0 have been used for food. The above values will be, however, specified on presenting the simulation results in the following “results and discussion” section.

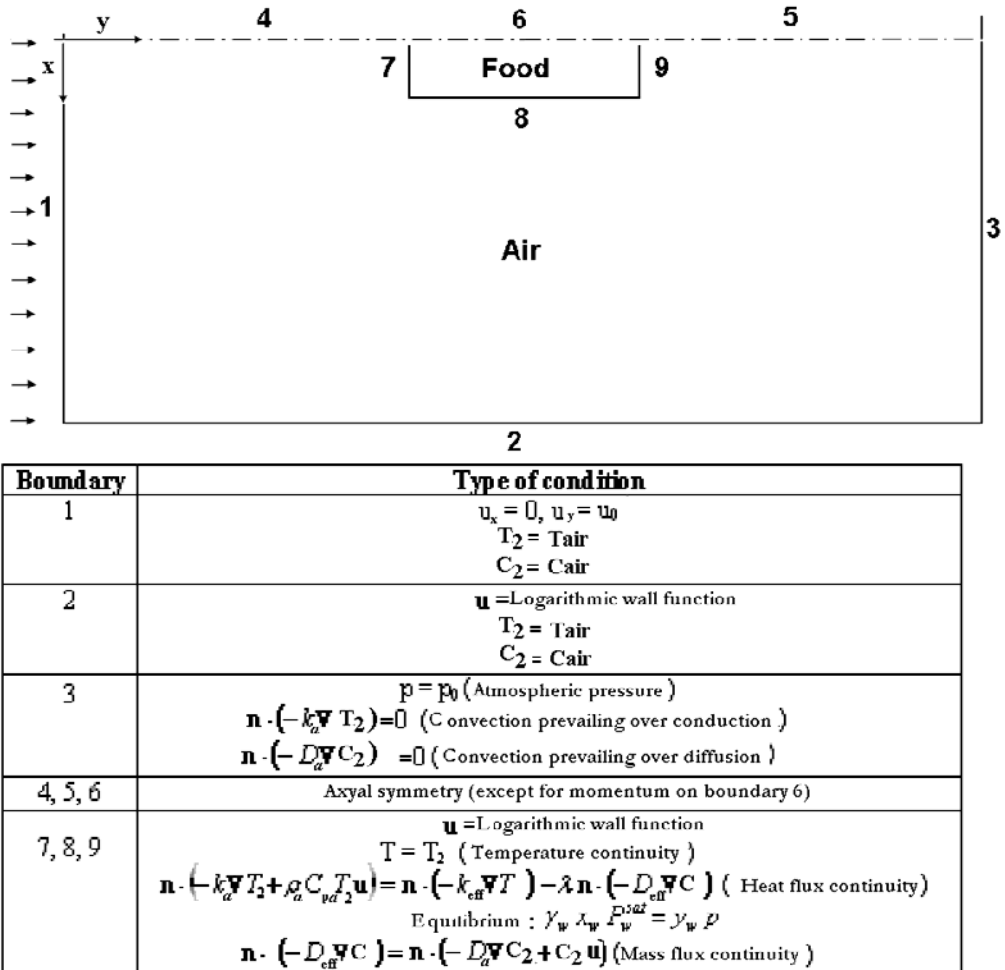


Figure 5. Boundary conditions used to formulate *mod2*.

As far as the boundary conditions are concerned, they are reported, for sake of brevity, in the fig. 5 where each different boundary has been identified by a number ranging from 1 to 9. Some of the above boundary conditions are straightforward; some others need a more detailed explanation. At the food-air interfaces (boundaries 7 - 9), where no accumulation occurs, the continuity of heat fluxes actually accounts for the fact that the heat transported by convection and conduction from air to food is partially used to raise sample temperature by conduction and partially to allow water evaporation. The latter effect is described by considering water latent heat of vaporization (λ) that is expressed in terms of the interfacial food temperature and of its moisture content (Ruiz-López, Córdova, Rodríguez-Jimenes, García-Alvarado, 2004):

$$\underline{n} \bullet (-k_a \underline{\nabla} T_2 + \rho_a C_{p_a} T_2 \underline{u}) = \underline{n} \bullet (-k_{eff} \underline{\nabla} T) - \lambda \underline{n} \bullet (-D_{eff} \underline{\nabla} C) \quad (19)$$

On the same boundaries, a balance between the diffusive flux of liquid water coming from the product core and the flux of vapor that leaves the food surface and is transported, by both diffusion and convection, into the drying air applies:

$$\underline{n} \bullet (-D_a \underline{\nabla} C_2 + C_2 \underline{u}) = \underline{n} \bullet (-D_{eff} \underline{\nabla} C) \quad (20)$$

Also in this case, an equilibrium relationship between the water concentration in the air and the water concentration, on the food surfaces actually exposed to the drying air (eq. 10), applies.

On boundary 2, it has been assumed that air temperature and its concentration are the same as those measured at the drier inlet section. These two conditions are valid under the hypothesis that the penetration of both temperature and concentration profiles is, actually, confined in two very thin regions that develop close to the food-air interface. In the following, the above assumptions will be validated (or falsified) on discussing the simulations results.

At the oven outlet section, conduction and diffusion phenomena can be neglected with respect to convection (Danckwerts conditions). As far as the boundary conditions referred to the momentum balance on the solid surfaces are concerned, a two-velocity scale wall function was used, as reported by Lacasse, Turgeon and Pelletier, 2004.

The above system of non-linear Partial Differential Equations, together with the above-described sets of initial and boundary conditions, has been solved by Finite Elements Method. Both the domains were discretized into a total number of 5846 triangular finite elements, leading to about 60000 degrees of freedom. Fig. 6 shows a detail of the considered mesh. On a Pentium IV computer running under Linux, a typical drying process duration of 5 hours was simulated, on average, in about 1 hour also in this case by the commercial package Comsol Multiphysics 3.3, using a time-dependent nonlinear direct solver already implemented in the same package.

Results and Discussion

The analysis of transport phenomena henceforth presented will be based on the examination either of some characteristic average variables or of temperature and concentration profiles. Simulations at different drying conditions have been performed to show how air characteristics affect food drying process and, hence, the drying time. In order to properly explain the physical meaning of the obtained results, it will be necessary to bear in mind the general considerations on drying process already described at the beginning of the present chapter. In particular, fundamental parameters like the wet bulb temperature, the difference existing between free and bound water and their relationship with the activity coefficient, the drying rate, the driving force, etc. will be often mentioned so to precisely interpret the behavior of drying process. Starting from a reference case, different simulations have been performed varying every single air property (i.e. the inlet temperature, its relative humidity and the feed velocity) in a specific range, typical of food drying process. To define the reference case, it has been assumed that the food sample, i.e. a 6-cm-long carrot slice with a

half-thickness of 0.5 cm, had an initial temperature equal to 283 K and an average initial moisture content (on a wet basis), $\overline{U}_0$, of 0.88 Kg/Kg, corresponding to an average initial moisture content (on a dry basis), $\overline{X}_0$, of 7.3 Kg/Kg. The drying air entering the oven had a uniform feed velocity of 5 m/s; in the tested range of operating conditions, turbulent conditions are attained with Reynolds numbers, within the drier, well higher than 10^4 . Finally, it was supposed that at the drier inlet section air had a dry bulb temperature, T_{gb} , of 343 K and a relative humidity, U_r , of 30%.

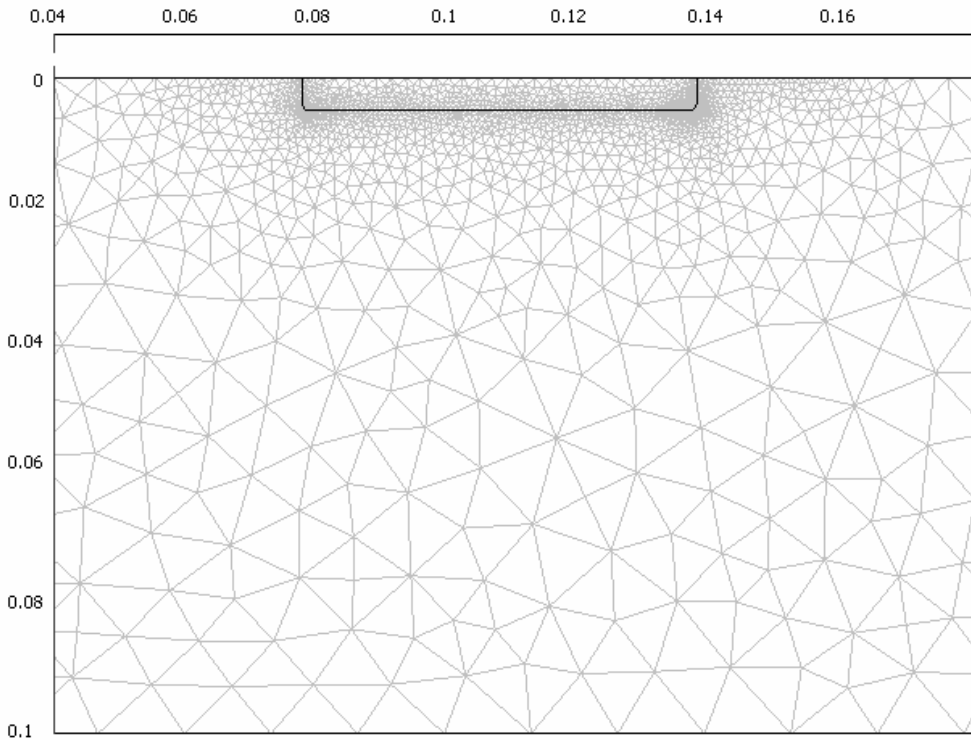


Figure 6. Discretization of food and air domains into triangular finite elements (detail of the mesh).

In the following, it will be sketched a comparison among the predictions that can be obtained simulating the drying process behavior by means of the simplified model, based on the utilization of literature transport coefficient and henceforth identified as *mod1*, and of the more complete approach that accounts also for the transport phenomena occurring in the drying air and that will be henceforth indicated as *mod2*. As far as *mod1* is concerned, it should be again observed that the utilization of a particular set of semi-empirical correlations for heat and mass transfer coefficients evaluation is critical to ascertain the model capability to predict the time evolutions of temperature and moisture content within the food. The model predictions, in fact, may significantly differ if two distinct choices of semi-empirical correlations, equally acceptable for the same drying problem, are performed. This aspect has, generally, deep repercussions on food processing. Wrong predictions of real system behavior might lead to stop drying process despite, for instance, of local moisture content that is still so high to promote microbial spoilage or might suggest to adopt operating conditions that,

actually, produce local damages in the food structure, thus determining a poor product quality. In the present analysis, *mod1* makes use of three different correlations, one for each of the surfaces exposed to drying air, to evaluate the local values of heat transfer coefficients from the Nusselt number, Nu , expressed in terms of characteristic Reynolds, Re , Prandtl, Pr , and Grashof, Gr , numbers (Perry & Green, 1984, Welty, Wicks, Wilson, Rorrer, 2001):

Table 1. Semi-empirical correlations used to estimate heat transfer coefficients on each food surface

Boundary	Semi-empirical relationship	Definition of dimensionless numbers
Impact surface (identified as boundary 7)	$Nu_x = 0.25 Re_x^{0.588} Pr^{1/3}$	$Nu_x = \frac{h_{x 7} \cdot x}{k_a}$; $Re_x = \frac{\rho_a \cdot u_0 \cdot x}{\eta}$
Surface parallel to air flow (identified as boundary 8)	$Nu_y = 0.648 Re_y^{0.5} Pr^{1/3}$	$Nu_y = \frac{h_{y 8} \cdot y}{k_a}$; $Re_y = \frac{\rho_a \cdot u_0 \cdot y}{\eta}$
Rear surface (identified as boundary 9)	$Nu_x = 0.59 (Pr \cdot Gr_x)^{1/4}$	$Nu_x = \frac{h_{x 9} \cdot x}{k_a}$; $Gr_x = \frac{x^3 \cdot \rho_a \cdot g \cdot \Delta \rho_a}{\eta^2}$

The Prandtl number is defined as $Pr = \frac{C_{pa} \cdot \eta}{k_a}$. In the previous relationships, x and y

define the local position on each of the food surfaces; $h_{(x,y)|i}$, characterized by a numeric subscript (i) corresponding to each boundary, is the local value of heat transfer coefficient; u_0 is air velocity at the inlet section of the drier; g is the acceleration gravity. All the physical and transport properties defining each dimensionless numbers have been evaluated at film conditions (the subscript f has been omitted).

It should be observed that, as far as the rear face of food sample is concerned, the Nusselt number has been actually expressed in terms of Grashof number since it can be supposed that air circulation in proximity to boundary 9 is so limited that free convection prevails over forced convection.

Once the heat transfer coefficients have been estimated, the Chilton-Colburn analogy is used to calculate the mass transfer coefficients referred to each corresponding boundary (Perry & Green, 1984).

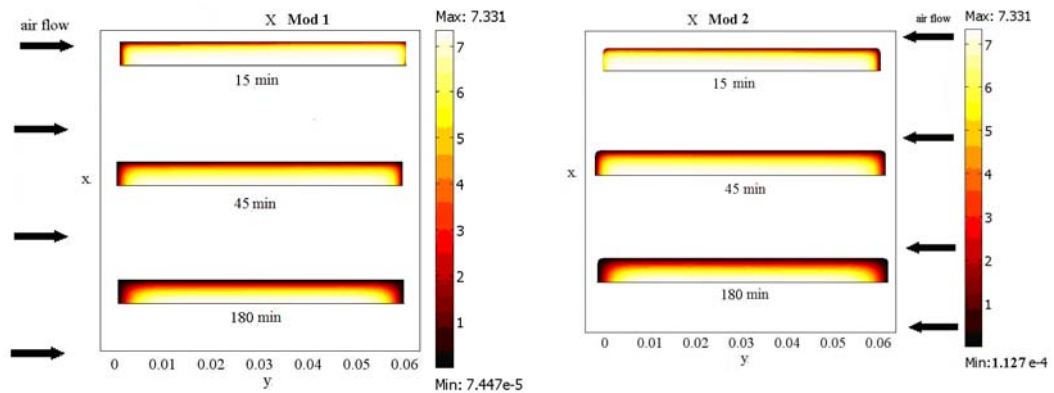


Figure 7. Profiles of food moisture content (on a dry basis) obtained by both the models.

It should be preliminary observed that several authors, as reported by Saravacos and Maroulis, 2001, made use of the same semi-empirical correlation to estimate, for all the exposed surfaces, the Nusselt number as a function of a unique average Reynolds number. This choice might be responsible for very inaccurate predictions of the real transfer rates at the food/air interfaces since each of the surfaces or, actually, each point of a surface is characterized by different fluid-dynamic conditions that have a strong influence on the external resistances to both heat and mass transfer.

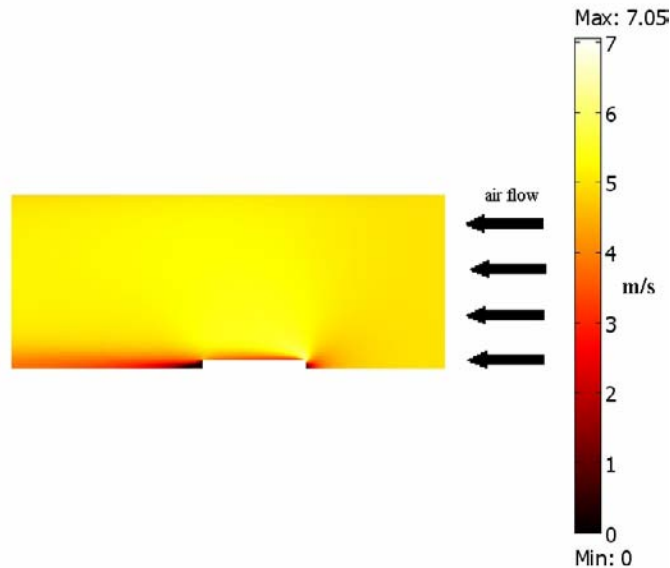


Figure 8. Air velocity field in the drying chamber.

The following fig. 7 shows a comparison of food moisture content profiles (on a dry basis) that are obtained by both *mod1* and *mod2* after 15 minutes, 45 minutes and 3 hours from drying beginning. It has been assumed that drying air had a temperature of 343 K, a relative humidity of 10% and an inlet velocity of 5m/s. In these conditions the wet bulb temperature is equal to 307.6 K (Perry & Green, 1984). The food surface upon which air impinges is heated more rapidly than the other surfaces and its temperature suddenly rises above the wet bulb temperature, thus initiating the water removal. The impact surface is interested by two different simultaneous phenomena: 1) the heat transferred from air provides both the latent heat of vaporization necessary for water evaporation and the heat necessary to increase, by conduction, the temperature of food dry matter; 2) the drying rate is very high and involves the free water that, therefore, vaporizes and is immediately transported into the air. Both *mod1* and *mod2* are capable to predict the different transport rates of water that are achieved on each exposed surface. The water removal is responsible for the movement of dry/moist interface toward the food core. This displacement is more rapid from the surface where drying air impinges and is rather slow, especially in the very initial stage of the process, from the opposite side. The rear face of food, in fact, is interested by a rather wide “segregation” region that forms due to an ineffective air circulation, as it is confirmed by the velocity field reported in fig. 8, and that determines a significant delay on reaching the wet bulb temperature necessary to initiate free water removal. This result, found over the whole

range of tested velocities, confirms that heat transfer near the back surface of food sample occurs mainly by free convection. It should be also observed that if a unique semi-empirical correlation had been used to estimate the Nusselt number, an identical behavior of all the exposed surfaces would have been observed. This would have determined an equal displacement of the so-called dried front from the outer regions to the food core; a result that, obviously, conflicts with the physical experience about the phenomenon under consideration.

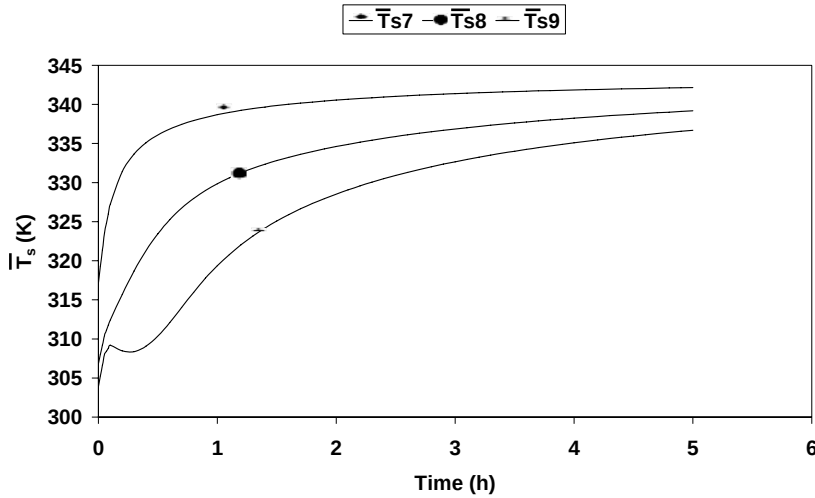


Figure 9. Time evolutions of food average temperature on each of the exposed surfaces (air temperature 343 K, relative humidity 10%, inlet air velocity 5 m/s).

The time evolutions of food surfaces temperature, averaged over each of the surfaces and evaluated as a function of drying time ($\bar{T}_s(t)$) by *mod2*, are reported in fig. 9. The food surface upon which air impinges (boundary 7) is heated more rapidly than the other surfaces and its temperature rises, quickly, above the wet bulb temperature. This behavior is definitely to be ascribed to the flow conditions. The impact surface is interested by two different simultaneous phenomena: 1) the heat transferred from air provides both the latent heat of vaporization necessary for water evaporation and the heat needed to increase, by conduction, the temperature of food dry matter; 2) the drying rate is very high and involves the free water that, therefore, vaporizes and is immediately transported into the air. A completely different behavior can be observed on the opposite site, i.e. on boundary 9, where, at the very beginning of drying process, the heat transported from air increases food temperature up to the wet bulb temperature; later on, the average temperature profile has a nearly constant value. During this stage, whose duration depends on the operating conditions, the heat transferred from air provides only the latent heat of vaporization to free water. When also bound water begins to be removed, the heat transported by convection and conduction from air to food is partially used to raise sample temperature by conduction and partially to allow water evaporation. Average temperature now increases up to a plateau value, with a slope depending on the operating conditions. The behavior of the food surface parallel to the main direction of air flow can be considered as “intermediate” between the other two boundaries. Temperature profiles are characterized by a nearly constant value, but its duration is shorter

or does not actually exist when, like in the present case, velocity field is so high to determine a significant reduction of transport resistance external to food sample.

In the following the effects of air characteristics on the drying rates predicted by both the models will be shown. As a general consideration, it should be remarked that, among air characteristics, velocity has a strong influence on the transport resistances outside the food sample and, therefore, on the transfer rates of both heat and water at food-air interface. Temperature and humidity of air entering the dryer mainly affect the available driving forces promoting transport phenomena between food and air.

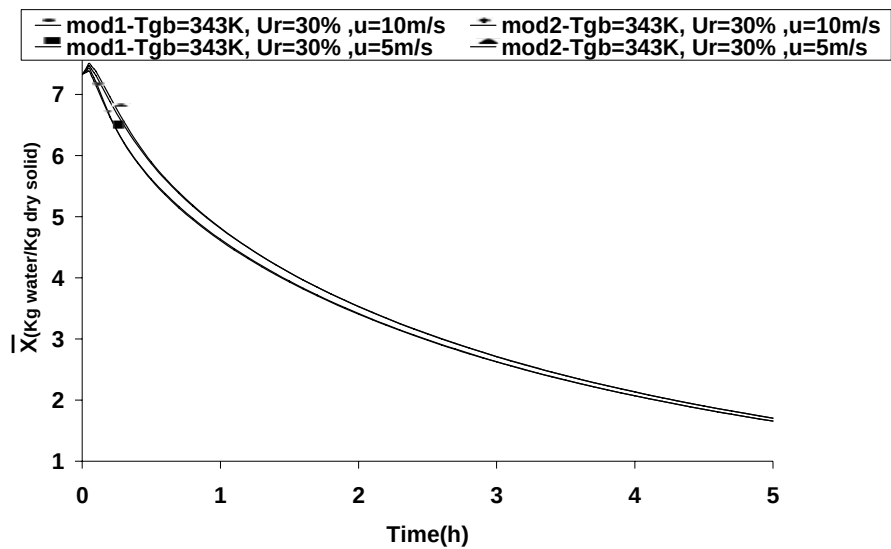


Figure 10. Average food moisture content as predicted by both the models (effect of air inlet velocity).

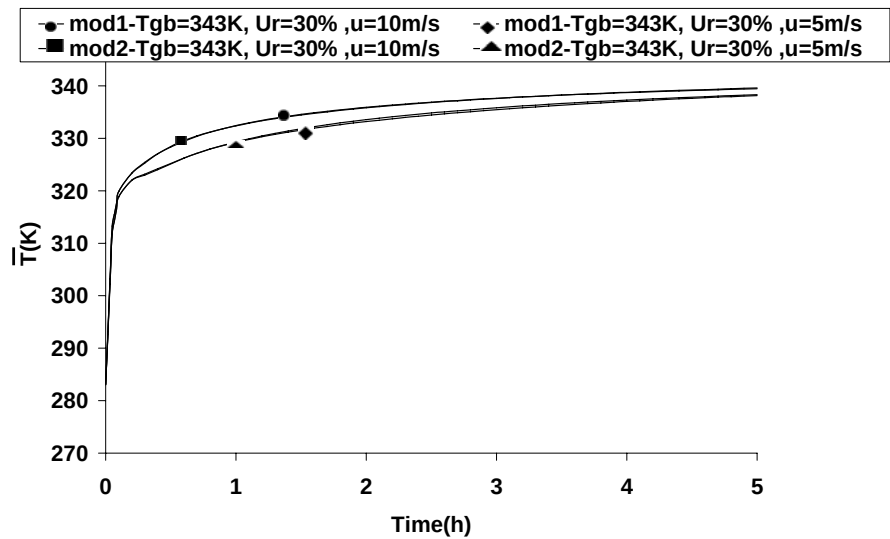


Figure 11. Average food temperature as predicted by both the models (effect of air inlet velocity).

Actually, an increase of air velocity corresponds to a decrease of external resistances to heat and mass transfer. This effect is however significant only when internal resistances do not control the overall rate of the process. Therefore, the improvement related to higher values of feed velocity can be observed only when free water evaporates and leaves the food. As soon as bound water is also removed, internal resistance to mass transfer predominates and air velocity has a weak influence on process rate; during this stage the value of effective diffusivity of water in food and its dependence on both temperature and food moisture content actually control the drying rate. Figs. 10 and 11 show the predictions obtained, by both the models, when drying process is performed by an air temperature of 343 K, a relative humidity of 30% and two different feed velocities equal to 5 and 10 m/s, respectively. In the above conditions the wet bulb temperature is 321 K (Perry & Green, 1984). The results are presented in terms of food moisture content (on a dry basis), averaged over the whole food sample and evaluated as a function of drying time, $\bar{X}(t)$, and of food temperature, averaged over the whole food sample and evaluated as a function of drying time, $\bar{T}(t)$. In the tested cases both the models give very close predictions and a slight difference can be noted only during the very initial stage of drying process. An improvement of drying rate is observed as air velocity is increased, even though the curves tend to approach each other as soon as the internal resistances prevail over the external ones. The initial steep temperature rise shown in Fig. 11 is, actually, the result of two different contributions. In fact, heat transfer depends on both the convection (due to the temperature difference between air and the solid surface), and, as long as food surface temperature is lower than the wet bulb temperature, the latent heat (due to the condensation of the vapor on food surface). Vapor condensation is also responsible for the corresponding initial slight increase of total food moisture shown in fig. 10. Once wet bulb temperature is attained, water concentration at food-air interface, C_i , exceeds the value of bulk concentration of water in air that, depending on air temperature and its relative humidity only, can be assumed as constant throughout all the process; water evaporation, therefore, prevails over vapor condensation and heating rate decreases. Hence, while food temperature slowly increases towards air temperature value, food moisture content diminishes at a decreasing drying rate. Fig. 10 confirms that initially, when the process is controlled by external heat transfer and the water leaving the sample is not bound to food structure (*free water*) drying rate attains its maximum value. Afterwards, when the process rate is controlled by internal mass transfer and the water leaving the solid is bound to the food structure, a progressively decrease of drying curve slope is observed. A comparison between the results obtained by *mod1* and *mod2* shows, in the tested cases, that both the models predict a similar behavior. This could suggest that the proposed simplified approach is capable of giving as accurate predictions as the more complete model, as long as a proper set of transport coefficients is used.

Figs.12 and 13 show the predictions obtained by both the models when drying process is performed by an air temperature of 343 K that is fed to the drier at a velocity of 5 m/s; two different values of relative humidity, equal to 30% and 10%, have been chosen to test the models. In the above conditions the wet bulb temperature is equal to 321 K and to 307.6 K, respectively (Perry & Green, 1984). Also in this case, the results are presented in terms of $\bar{X}(t)$ and of $\bar{T}(t)$. When air relative humidity is changed from 10% to 30% a simultaneous

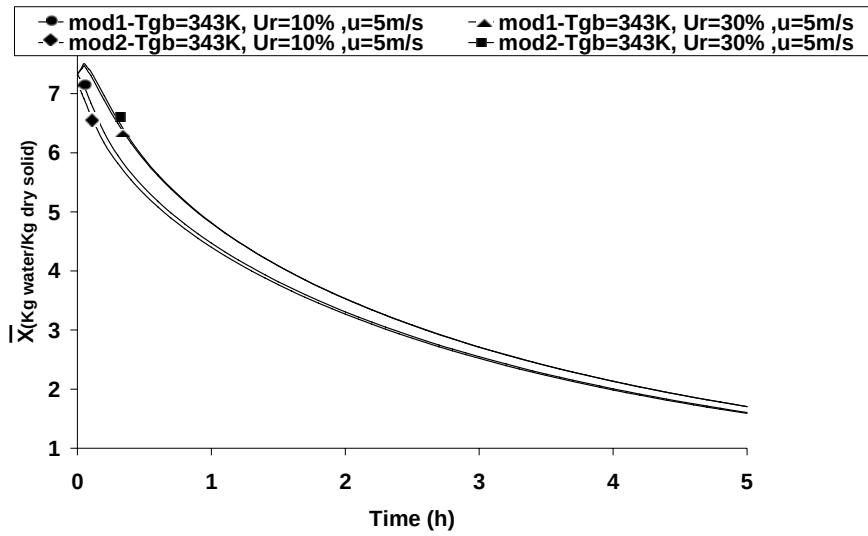


Figure 12. Average food moisture content as predicted by both the models (effect of air relative humidity).

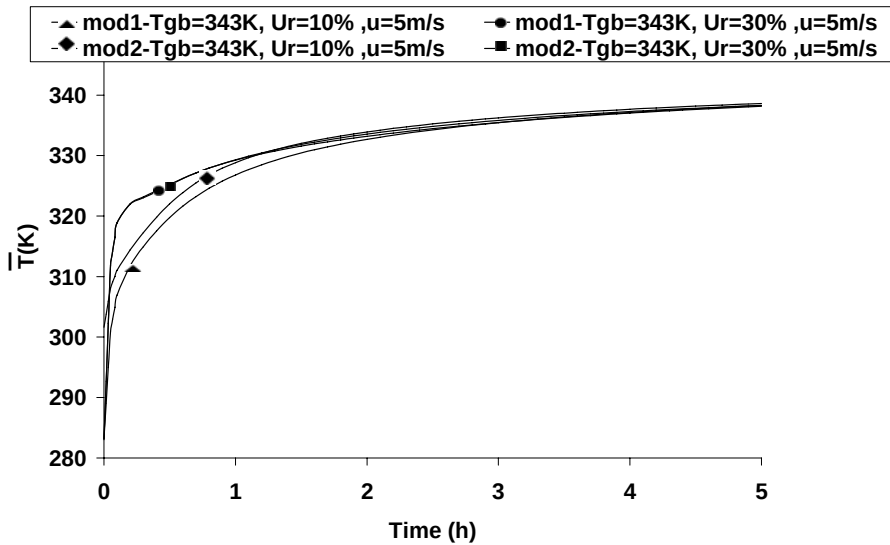


Figure 13. Average food temperature as predicted by both the models (effect of air air relative humidity).

increase of both the wet bulb temperature and of bulk water concentration, by a factor of about 3, is observed. An increase of relative humidity does, therefore, determine a lower drying rate and is also responsible for a longer time to initiate water removal. This behavior can be explained observing that, at the very beginning of the process, i.e. when free water is actually subtracted from the food, an increase of air relative humidity significantly lowers the drying rate owing to a reduction of the driving force promoting water transport. Moreover, it can be noted that vapor condensation does not occur appreciably when air relative humidity is

equal to 10% (fig. 12). When bound water is progressively involved in drying, internal resistance to mass transfer represents the actual limiting step and the concentration difference outside food sample affects the process rate only to some extent. A comparison between model predictions shows, in this case, that the two curves corresponding to the more drastic operating conditions differ, especially during the first two hours of drying process, for both $\bar{X}(t)$ and $\bar{T}(t)$. When food drying is performed under milder conditions, both *mod1* and *mod2* predict a similar behavior.

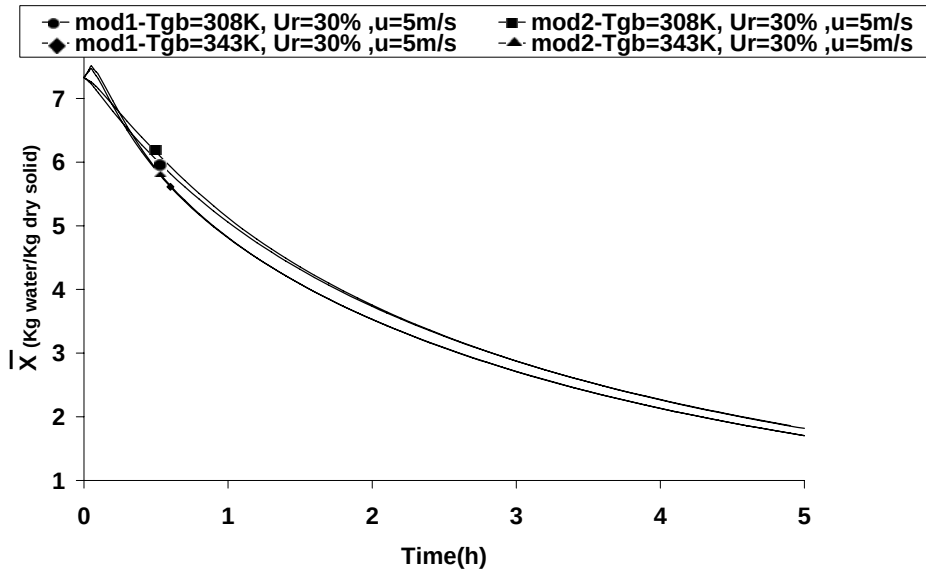


Figure 14. Average food moisture content as predicted by both the models (effect of air temperature).

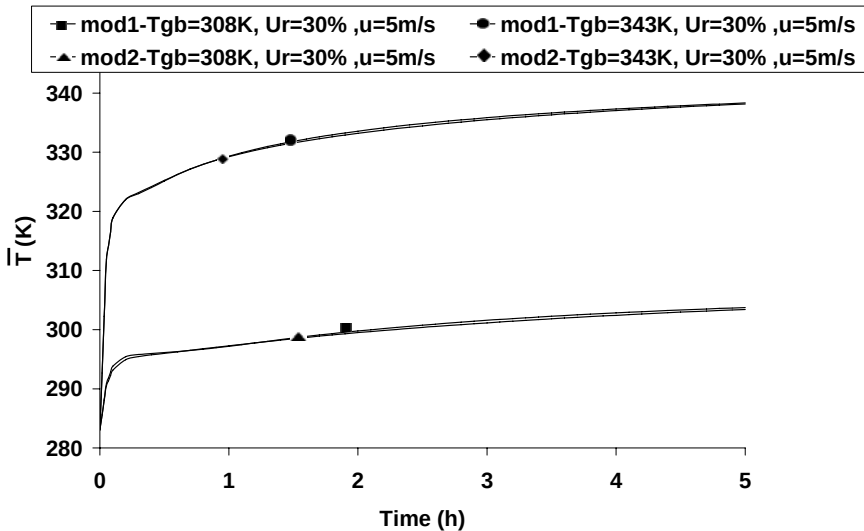


Figure 15. Average food temperature as predicted by both the models (effect of air temperature).

Figs.14 and 15 show the simulation results obtained by the two models when drying process is performed by a drying air having a relative humidity of 30 % that is fed to the drier at a velocity of 5 m/s; two different values of dry bulb temperature, equal to 308 K and 343 K, have been used to test the models. An increase of dry bulb temperature from 308 K to 343 K determines an initial delay of drying process beginning, due to the increase of wet bulb temperature from 295 K to 321 K, (Perry & Green, 1984). Also in this case, vapor condensation does not occur appreciably when dry bulb temperature is equal to 308 K (fig. 14). Moreover, under the same conditions of relative humidity, an increase of air temperature causes both a significant reduction of the driving force to mass transfer from food to air and an improvement of heat transfer from air to food. The observed rate of drying process can be, therefore, considered as a trade-off between different physical phenomena that determine a dependence on air inlet temperature mainly during the initial step of the process, where a higher operating temperature is actually responsible for a faster drying. The effect of temperature on drying performance is, instead, less important in the last part of the process, when internal resistance to mass transport prevails and represents, actually, the limiting step. During this stage, it can be observed from fig. 14 that drying rate is much slower and the slopes of each of the curves are almost the same. A comparison among model predictions shows, also in this case, that both the models predict a similar behavior, except during the initial stage of drying process performed at a temperature of 308 K, where *mod1* tends to slightly overestimate the process rate with respect to *mod2*.

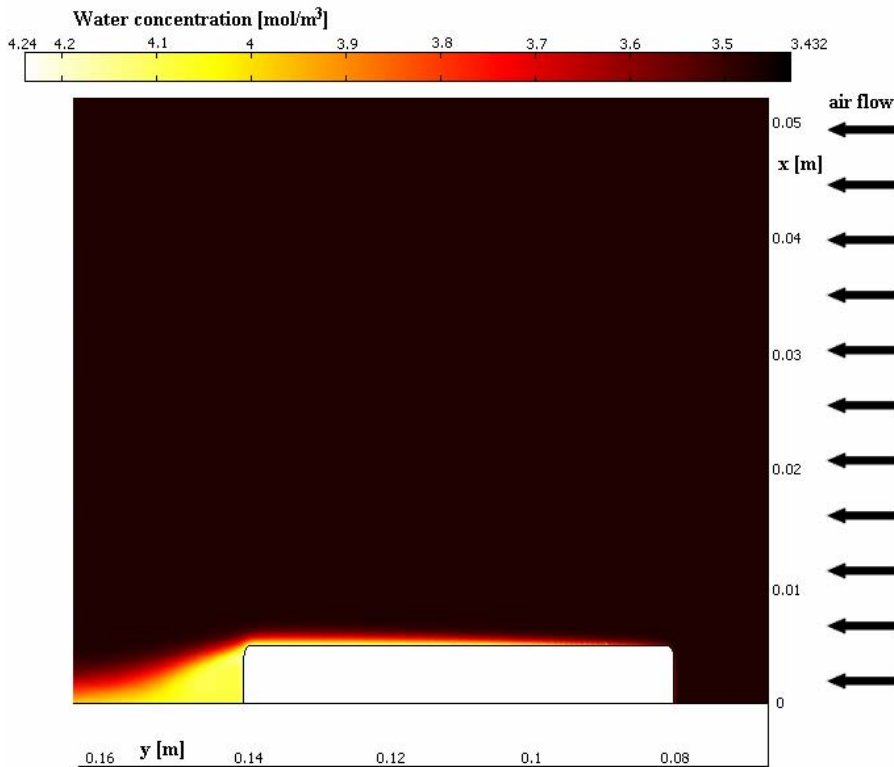


Figure 16. Water concentration profile in the air outside the food sample ($t = 15$ min).

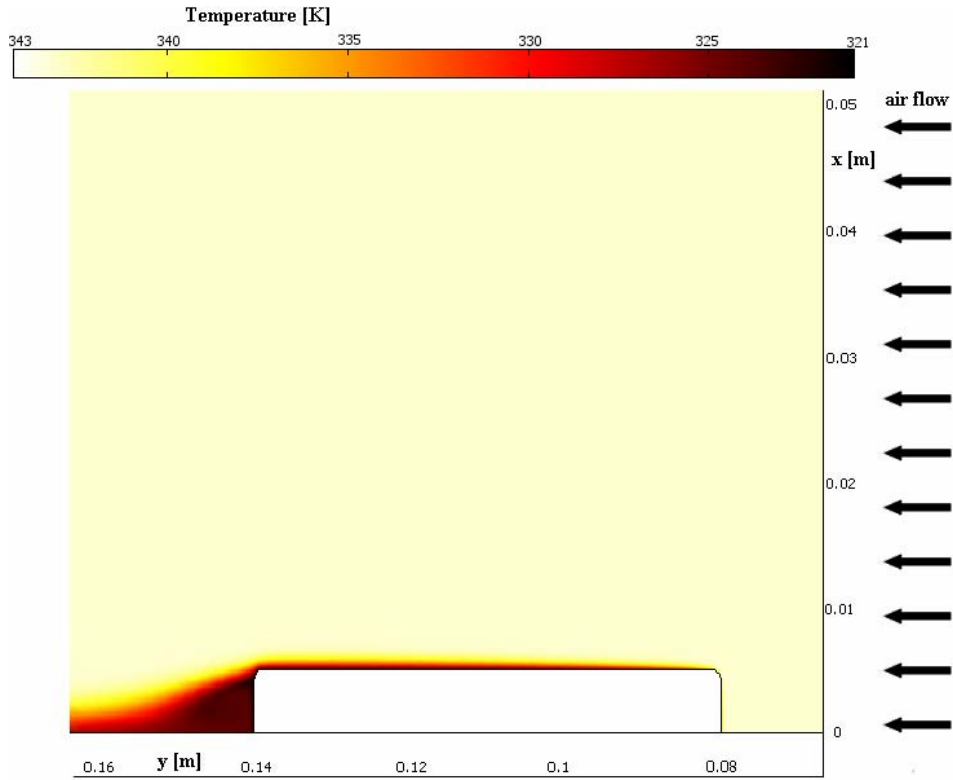


Figure 17. Temperature profile in the air outside the food sample ($t = 15$ min).

It is now interesting to analyze the following Figs. 16 and 17 that show, respectively, the distributions of water concentration and temperature profiles in the air after 15 minutes, obtained in the so-called reference case. It can be observed that both concentration and temperature gradients develop in two very thin regions close to the food surface whose thickness is very similar to that predicted, for instance, by the boundary layer theory (Schlichting, 1960). Figs. 16-17 confirm that some of the boundary conditions described in Fig.5 may be considered as a true representation of real system behavior, since both concentration and temperature gradients vanish at a very short distance from the food surface equal to about 3 mm compared to the dryer transverse dimension of 10 cm.

Before dealing with the last part of the present analysis that will regard the estimation of heat and mass transfer coefficients by means of *mod2*, it is now necessary to suggest some guidelines that might help deciding which of the two approaches is to be preferred. Actually, *mod1* is much simpler, it is capable of simulating a complete drying operation in just a few minutes and its predictions are in a very good agreement with the more complete model, i.e. *mod2*. Nevertheless, *mod1* is strongly dependent on heat and mass transfer coefficients that, generally, are known only for very simple geometries and for drying operations performed in a restricted range of process conditions. Moreover, it should be observed that *mod1* made use of different semi-empirical correlations for each of the surfaces actually exposed to the drying air. This practice is not so common in the literature, since it is usually preferred to utilize the same semi-empirical correlation to estimate, for all the exposed surfaces, the Nusselt number

as a function of a unique average Reynolds number. One of these correlations was proposed, for example, by Ratti & Crapiste, 1995:

$$Nu_L = 0.249 Re_L^{0.64} \quad (21)$$

the subscript L indicates that the characteristic length utilized to define the Reynolds number is the whole slab length, but it could be also the diameter (in the case of both a cylindrical-shaped and a sliced vegetable). It should be observed that the utilization a unique semi-empirical correlation is often dictated by the objective difficulties related to the experiments. These have to be performed to derive a proper set of transport coefficients, in a as wide as possible range of controlled conditions. In addition, a considerable number of the papers currently available in the literature do not account for the variation of heat and mass transfer coefficient with the local position. At this point of the analysis, it is interesting to compare, in some typical situations, the predictions obtained by the same model, i.e. *mod1*, when either eq. 21 or the semi-empirical correlations reported in Tab. 1 are adopted to simulate drying process. The Chilton-Colburn analogy has been used to calculate the mass transfer coefficient starting from the estimated values of heat transfer coefficients.

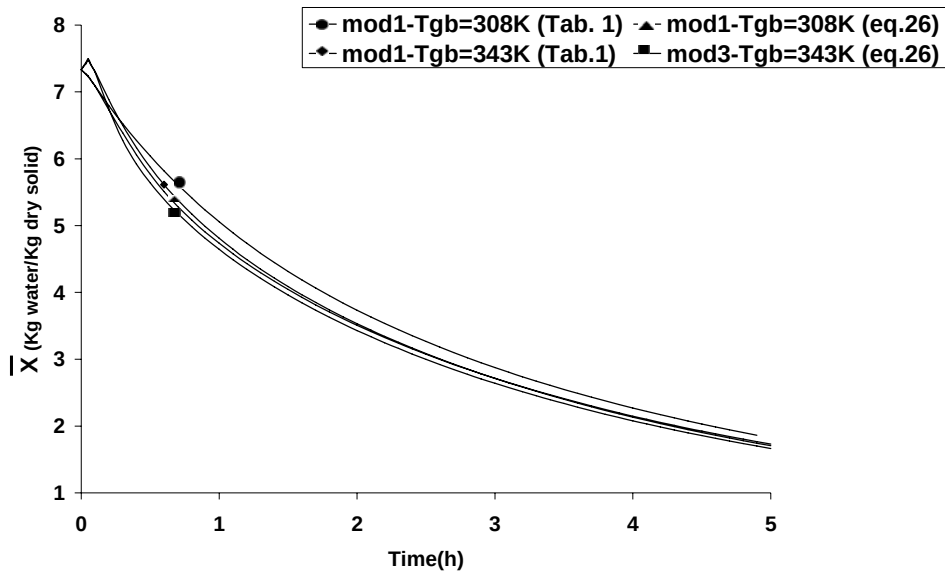


Figure 18. Effect of semi-empirical correlations on average food moisture content in two different cases ($U_r = 30\%$, $u = 5$ m/s).

Figs. 18 and 19 show this comparison when two different values of dry bulb temperature and of air velocity are chosen to perform the simulations. Significant differences can be observed in all the tested conditions. The utilization of a unique correlation is responsible for a major overestimation of operating conditions effects on the drying rate. The general trends are not significantly affected by the values of semi-empirical correlations, but a rather lower value of food moisture content is calculated when the unique correlation is adopted, for both the considered velocities. The observed differences are actually more evident during the first

two hours of the process, but persist, to a lesser extent, also till the end of simulations. This behavior definitely does not depend on the model formulation and is to be ascribed only to an incorrect choice of semi-empirical correlation. Especially for the rear food surface, eq. 21 estimates a heat transport coefficient and, on the basis of Chilton-Colburn analogy, also a mass transfer coefficient that is not as high as that predicted. The results shown in Figs. 18-19 are meaningful since they confirm that the choice of a proper set of transfer coefficients is, actually, critical when drying process is to be simulated.

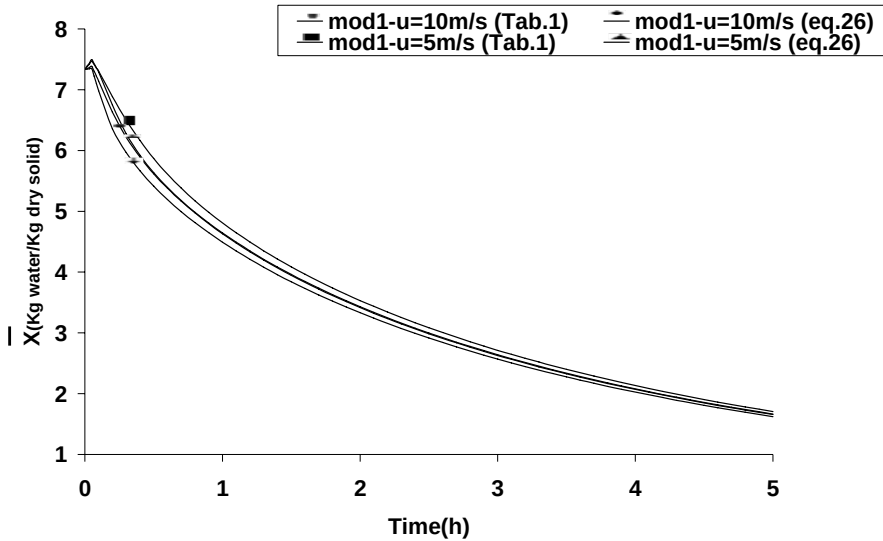


Figure 19. Effect of semi-empirical correlations on average food temperature in two different cases ($T_{gb} = 343\text{ K}$, $U_r = 30\%$).

On the basis of the above discussion, it seemed that *mod1* - provided that a proper set of semi-empirical correlation is actually available for the process under investigation - is to be preferred to *mod2* due to its simplicity, to the accuracy of its predictions (in most of the tested cases) and to the low computational effort that is needed to perform numerical simulations. *Mod2*, however, was developed to analyze drying process from a more general point of view that could be particularly useful in those conditions (irregular food shapes, operating variables changing with time, etc.) for which it might be rather difficult either to find literature correlations or to estimate them as a result of suitable and accurate experiments. *Mod2* has certainly a wider range of validity and, although more complicated and computationally more onerous, provides a more precise description of the actual system behavior than *mod1*.

One of the potentialities of *mod2* definitely concerns its “ability” to calculate the transport coefficients at food/air interfaces. This calculation is performed by means of fundamental considerations only and without resorting to any empirical correlation. For example, the local mass transfer coefficients at each surface can be calculated once both the molar diffusive flux of water and a characteristic concentration difference are obtained as a result of the above-described systems of PDEs (eqs. 2-3 and eqs.11-18). The following definition can be used to estimate the local values of mass transfer coefficient, $k_c(y)$, at the food surface parallel to the main flow of drying air (Bird, Stewart, Lightfoot, 1960):

$$k_c(y) = \frac{-D_a \frac{\partial C_2(x, y)}{\partial x} \Big|_{x = \text{food surface}}}{C_i(y) - C_{gb}} \quad (22)$$

Both the numerator and the denominator of eq. 22 are obtained as a result of each numerical simulation, so they directly account for the actual values of the operating variables chosen to analyze drying process behavior in each situation.

Similar considerations can be done to estimate the mass transfer coefficients at the other two exposed surfaces, but also to calculate heat transfer coefficients, h , once both heat flux and a characteristic temperature difference are known at each position of food surfaces.

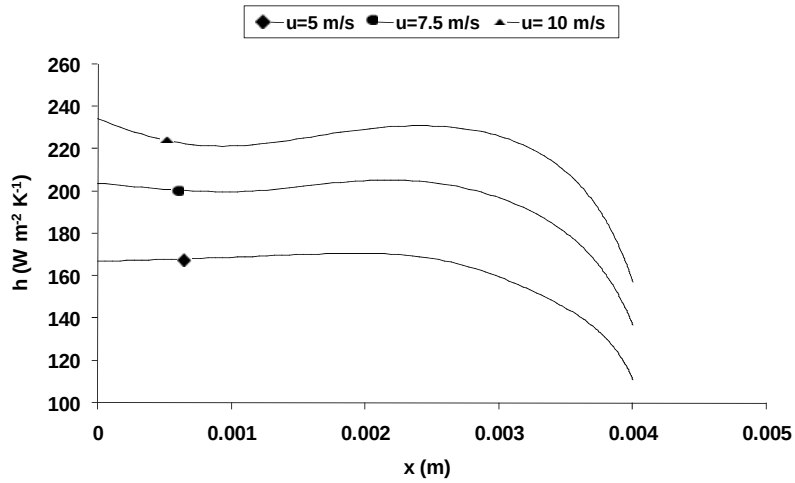


Figure 20. Local values of heat transfer coefficient on the food surface where air impinges (effect of inlet velocity).

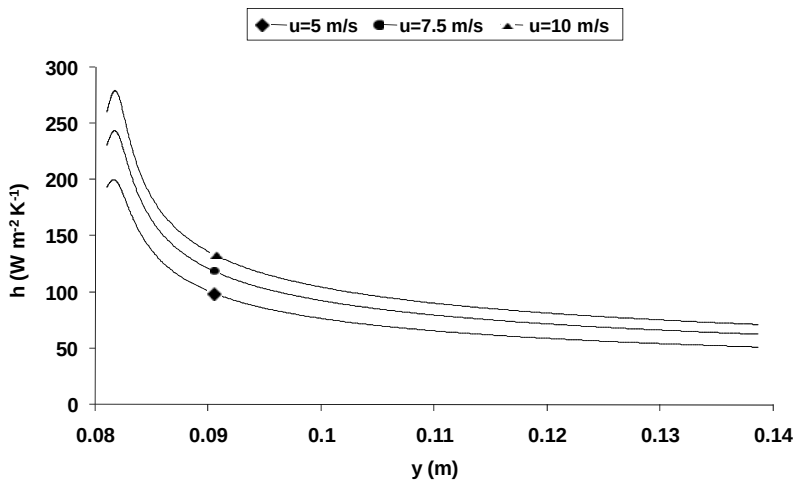


Figure 21. Local values of heat transfer coefficient on the food surface parallel to air flow (effect of inlet velocity).

Figs 20 and 21 show the local values of heat transfer coefficient evaluated, after one hour of drying, on the food surface where air impinges and on the surface parallel to air flow, respectively. Three different values of air velocity have been tested (5, 7.5, 10 m/s) with a dry bulb temperature and an air relative humidity equal to 343 K and 30%, respectively. It should be again remarked that heat and mass transfer coefficients play a significant role when *free water* is actually removed from food and the controlling mechanism is the external transport of both heat and water. When external transport limits drying rate any variation of either air characteristics or fluid-dynamic conditions can lead to a great improvement or, conversely, to a significant worsening of both drying and heating rates. As it is shown in Figs. 20-21, impact surface has much higher values of transfer coefficients than the food surface parallel to air flow. Moreover, air velocity is responsible, as expected, for a significant variation of heat transfer coefficient that is, on average, 38% higher when feed velocity increases from 5 to 10 m/s. Similar considerations can be done about the mass transfer coefficient that is shown, for the food surface parallel to air flow only, in Fig. 22. It should be observed that the local values of k presented in Fig. 22 are not the result of the application of Chilton-Colburn analogy, but come directly from the solution of PDEs 7-18 coupled to PDEs 2-3. Nevertheless, by a comparison of the numerical results shown in Figs. 21-22, it can be verified that Chilton-Colburn analogy actually applies since the following relationship (Bird, Stewart, Lightfoot, 1960) is satisfied:

$$\frac{h}{k_c} = \frac{\rho_a C_{pa}}{C_{tot}} \left(\frac{Sc}{Pr} \right)^{2/3} \quad (23)$$

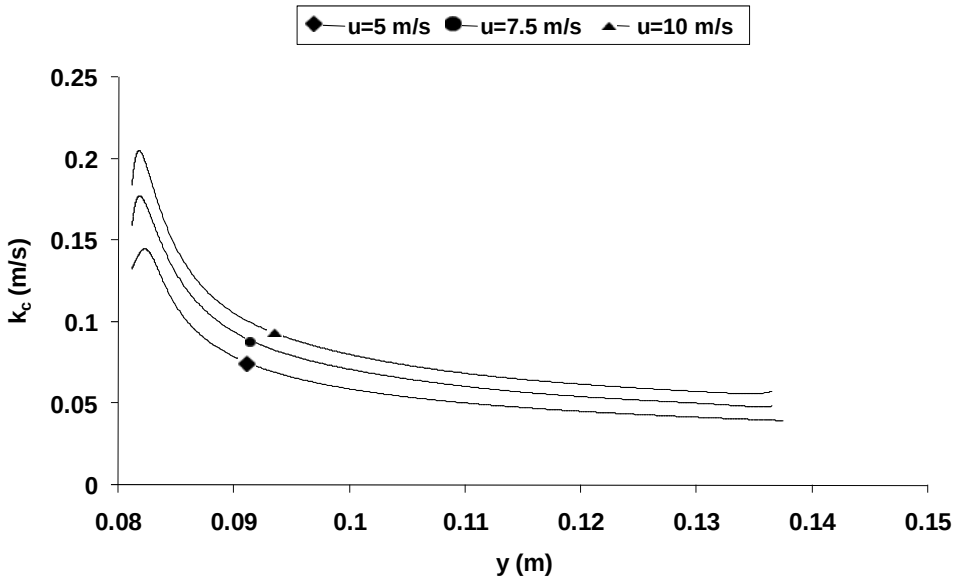


Figure 22. Local values of mass transfer coefficient on the food surface parallel to air flow (effect of inlet velocity).

Model Validation

In addition to the numerical simulations carried out on a bidimensional flat system and described in the previous sections, some others were performed with the specific aim of verifying the model validity. This has been achieved checking the agreement between the experimental results obtained with reference to the drying, by air, of cylindrical-shaped carrots and the model theoretical predictions attained by means of *mod2*. The general transport equations (2–3 and 7-18) and their corresponding boundary conditions have been converted (Bird, Stewart, Lightfoot, 1960) to account for the cylindrical-shaped geometry of both food sample and lab-scale drying apparatus. Fig. 23 shows, in two different situations, the comparison between experimental and predicted food moisture content during two drying tests performed at the same value of air velocity (1.11 m/s) but changing inlet air temperature and its humidity. In the milder condition, dry bulb temperature was maintained at 308 K and air relative humidity was equal to 22%; in the more severe case, air temperature was of 320 K and air relative humidity was equal to 16%. The comparison shows that, in the first case, the relative error never exceeds 4% while, in the second case, it is even lower and never larger than 2.6%.

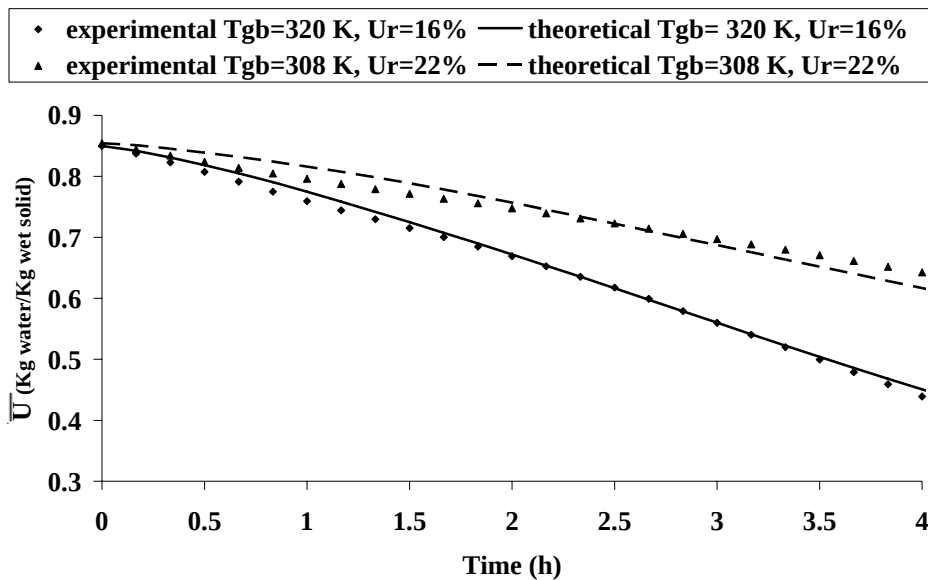


Figure 23. Comparison between model predictions and experimental data - Dynamic evolution of food moisture content ($u=1.11\text{ m/s}$, $T_0=16^\circ\text{C}$).

Conclusion

In the present contribution it has been shown that mathematical modeling represents a very effective tool for the analysis of industrial transformations, such as food drying process. Two different models have been developed with the specific aim of determining if a much simpler approach, focused on the analysis of transport phenomena within the food only, is to be

preferred to a more complex analysis in which both the domains (food and air) are taken into account. Certainly, the latter approach is more general since it does not require the knowledge of any heat and mass transfer coefficient. For this reason, it is capable to simulate drying process also in those conditions for which either semi-empirical correlations are not currently available (complex food geometries) or operating conditions are changed during drying process. The simple model is capable of giving very accurate predictions in a quite short time, provided that a correct set of semi-empirical correlations is used to estimate heat and mass fluxes at the food/air interfaces. Nevertheless, the same model, strongly dependent on heat and mass transfer coefficients, fails when a wrong choice of semi-empirical correlations is performed since the actual transfers at the food/air interfaces are not correctly estimated.

Both the models can be improved to account for some phenomena that, in the present analysis, have been neglected. Both shrinkage effects and transport of water vapor, by diffusion, within the dehydrated material are definitely very important and, especially in some practical situations, may affect drying rate and, therefore, the quality of final product.

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Chapter 5

RESEARCH TRENDS IN MODELING, OPTIMIZATION AND CONTROL OF THE DRYING OPERATION

Gikuru Mwithiga

Biomechanical and Environmental Engineering Dept.
Jomo Kenyatta University of Agriculture and Technology, Nairobi, Kenya

Abstract

Drying food is an extremely sensitive operation that requires the proper monitoring and control of the heating medium temperature as well as the length of time that the product is exposed to this temperature. Since the different food products have different heat sensitivity the heat load tolerance during drying cannot be generalized if loss of quality is to be avoided. On the other hand the drying process is a very high energy consuming operation and energy usage must be minimized without necessarily compromising on product quality. Optimization of a drying process requires that we consider the heat and mass transfer dynamics, product quality indices and production costs. Different control strategies and objective functions must be tried because it would not make business sense to produce a very high valued product at astronomical costs to the producer and nor would a low quality product sell simply because it is produced at minimum cost or energy consumption. This Chapter reviews first the research trends on modeling of the drying process based a heat and mass transfer, cost of drying and product quality. The strategic logistics that have been used over the years in attempts to optimize the drying operation have also been reviewed. Last but not least, the performance of these dryer control strategies in the practical optimization of the drying process have been discussed since it is how well a control strategies works that can make the entire optimization process either a success or a failure.

Introduction

Drying is an important aspect that occurs at one or more stages during the processing of many food products. Most cereals and legumes are harvested with high moisture content which has to be lowered if their preservation is to be assured. While large quantities of these products are dried under the sun some have to be dried artificially sometimes using very high temperatures. Also, in food processing factories, drying is highly evident especially in the

preparation of instant beverages and other food powders (Toledo, 2007; Bakker-Arkema, 1984).

Due to the characteristics of the product to be dried and the effect of both the dryer and drying medium parameters, the drying operations has to be properly controlled in order to optimize the performance of the entire production system. The decision on how to carry out the drying operation can be based on the cost of producing one unit of the product or on the returns from investment over a given period of time. Sometimes however the aim is to produce the highest quality product. This decision has to be made by management and is partly based on consumer demand. In most cases the solution would lie in between the two extremes (Houben et al., 2004; Fuller and Chater, 1997; Mittal et al, 1984).

To arrive at this decision we normally have to use drying models to predict what is likely to happen under certain conditions and optimization techniques. The models generally will relate the quality of the product to the drying conditions while the optimization procedure will try to seek the best alternative drying method. Once the most suitable dryer settings are known a suitable controller which both monitors and controls the conditions must be installed. The controller can only optimize the operation if it can maintain steady conditions of the desired outcome and respond to variations promptly (Douglas et al., 1992; Moreira and Bakker-Arkema, 1990).

For the purpose of producing a quality product under the best drying conditions there are three major areas that need to be thoroughly understood.

- a) Product quality aspects
- b) Dryer modeling and optimization
- c) Dryer control strategies

1. Product Quality Aspects

In the process of drying a product its quality may be affected by the kinematic, static and dynamic parameters of the drying system. By measuring these parameters either directly or indirectly the relationship between the operating parameters and the quality of the resulting product can be established. Although there are indeed many parameter that affect the drying operation some of the more important and more widely researched are;

- a) relative humidity and temperature of the drying medium (air)
- b) length of exposure of product to a given heating medium temperature
- c) rate of moisture removal
- d) temperature of the product

The chemical and physical characteristics of a biological product are closely related to the above parameters and are bound to change with time as drying proceeds. Different biological products have different characteristics and drying conditions which might be suitable for a given commodity are not necessarily suitable for another.

Changes occurring in a product during drying include change in composition, colour and concentration, change in length, volume, density and surface area, and development of cracks (for higher rates of drying) and molds (for lower rates of drying). These changes can normally

be related to the condition of the drying media and to the drying product (Ramos et al., 2003; Sosulnikova and Shampanova, 1970).

Most of these quality factors are however difficult to quantify and cannot be monitored as the drying takes place (Karel, 1987). For instance it is not possible to sample coffee beans and determine how the “body” or liquor of coffee beans changes as it continues to dry and even when the beans are finally dried, roasted and ground determination of these quality factors can only be done by a panel (Mwithiga, 1997).

Sometimes it requires that several measurements be made in order to quantify a quality factor. This calls for the assigning of weights to separate measurements in order to develop an index which will be sensitive enough to simulate actual quality changes (Karel, 1987).

We now look at some product characteristic changes that occur in drying and how they can be related to quality.

1.1. Sorption and De-sorption Isotherm and Equilibrium Moisture Content

Biological materials are hygroscopic in nature and therefore possess the characteristic of picking up and giving up moisture to the surrounding environment. It is recognized that water in food is the most important factor in biological, biochemical and biophysical degradation. For a given condition of air temperature and relative humidity there exists an equilibrium relative humidity of the material. This humidity is the moisture content that the material would approach if left in the environment for a long time and is normally referred to as the equilibrium moisture content (M_e). When the moisture content of a material is below the M_e then the product will pick up moisture from the surrounding environment, a condition which is referred to as adsorption. The reverse of this condition is called desorption and occurs when a product is losing water to the surrounding air. When the values of the M_e are plotted against the relative humidity of the surrounding air a sigmoid curve (as shown in Fig 1) which may be a sorption or desorption isotherm develops. A hysteresis exists between the two isotherms with the desorption isotherm having higher values of M_e than those for adsorption under the same environmental conditions (Öztekens and Soysal, 2000).

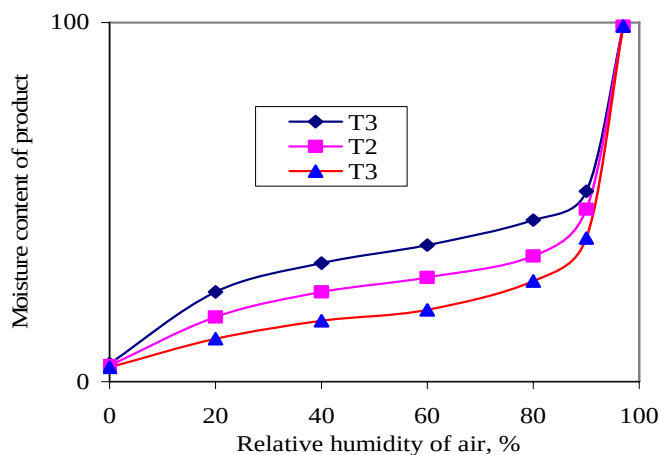


Figure 1. Typical isotherm curves of a biological product at different air temperatures where $T_1 < T_2 < T_3$.

Dehydration or removal of water to a suitable level allows the shelf life of the food to be extended from a few days to several months or even years. The hygroscopic property of the materials is therefore important during drying because it guides both the rate of drying as well as the final moisture content (M_e) under the drying conditions. When drying a product however, we need only remove enough water to reach the M_e of the product under normal storage conditions. Knowledge of the M_e of a product also allows us to determine the existing potential or ability to remove moisture from a substance which is the mass and heat transport phenomena during dehydration. The sorption enthalpy also allows us to determine the energy required to remove water from a material (Rizvi, 1986).

The hygroscopic property is however not present within the entire range of the moisture content of the material (Coppens and Wei, 1954) and it also changes with temperature. Some high moisture products exhibit an initial drying period during which the rate of water removal from the surface of the product remains constant as shown in Fig. 2. During this constant drying rate period, water evaporates freely from the surface of the material. For this to happen there must be free moisture on the surface and the rate at which moisture moves to the surface from the interior equals or exceeds the rate at which it evaporates from the surface. Hygroscopic behaviour starts when the material is able to develop its own vapour pressure at the surface which is in turn dependent on its moisture content, the saturation vapour pressure and vapour pressure of the surrounding air (Saravacos, 1986). The point at which this happens is called the critical point. Below the critical moisture content point, forces of water retention in the material come into play and as drying proceeds more units of energy are required to extract one additional unit of water.

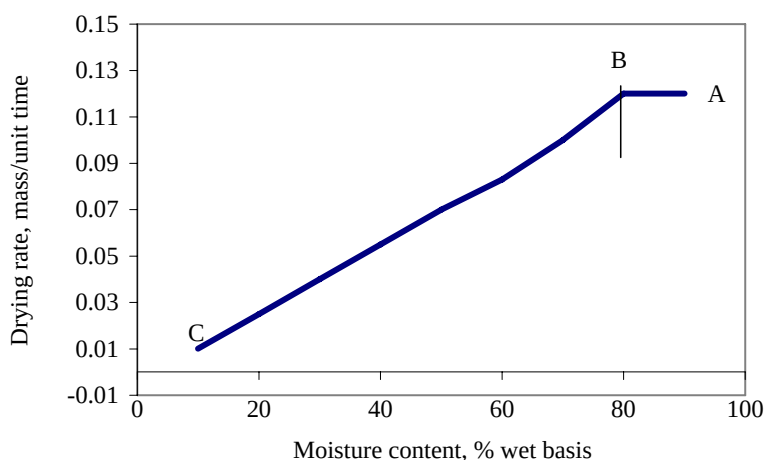


Figure 2. Drying of a biological product under both constant and falling rate period; AB constant rate drying, B critical point, BC falling rate drying.

The relationship between the energy required to evaporate water from a product at a specified moisture content can be expressed in the form of Eq.1. The vapour pressure (P_v) of the product at a particular moisture content can be measured easily in the laboratory. The saturated vapour pressure and the heat of vapourization of water from a free water surface are values that are easily available from engineering tables (Öztekens and Soysal, 2000). Therefore measuring the vapour pressure at different temperatures and moisture contents

allows us to produce the Othmer plots whose slope represent the ratio (h_{fg^*}/h_{fg}) as can be seen in Fig.3. This slope is always higher than unity but rarely exceeds 1.5 which means as expected that its more difficult to evaporate water from a biological product than it is to evaporate it from a free water body.

$$\ln(P_V) = \frac{h_{fg^*}}{h_{fg}} [\ln(P_{SV})] + C \quad (1)$$

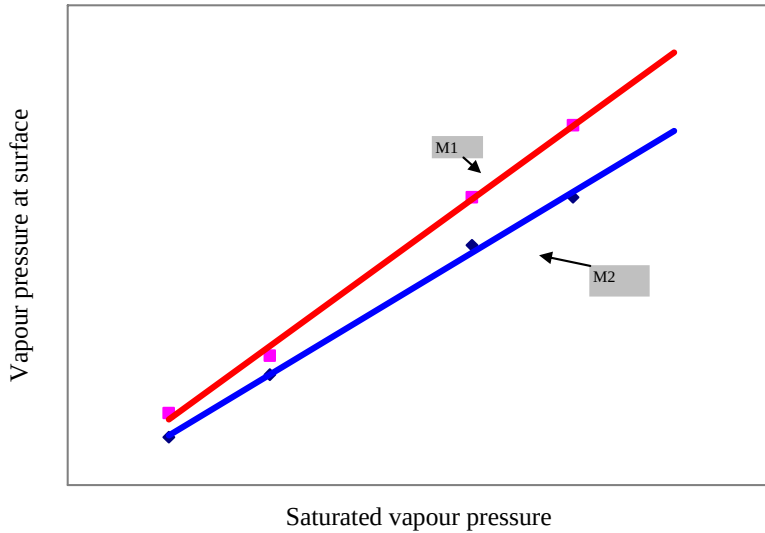


Figure 3. Variation of the vapour pressure at the surface of a biological product maintained at known moisture content (M) with change in the saturated vapour pressure of the surrounding environment ($M1 > M2$).

Researchers have also established that the energy required to evaporate one unit of water from a material increases as moisture content drops. As can be seen in Fig.4 more and more energy is required to evaporate one more unit of moisture from the product at lower moisture contents. The plot in Fig 4 can also be represented in the form of Eq.2 and then used to estimate the heat of vapourization in any given material provided that the constants have already be determined experimentally (Öztekins and Soysal, 2000; Rizvi, 1986).

$$\frac{h_{fg^*}}{h_{fg}} = 1 + C_1 \exp(-C_2 M) \quad (2)$$

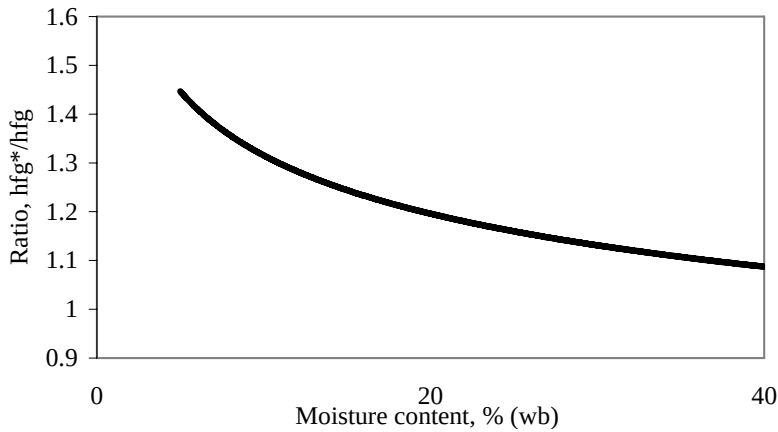


Figure 4. Variation of the heat of vapourization with the moisture content of a biological product.

It is generally accepted that the hygroscopic property of a biological material is a function of moisture content, temperature of product, relative humidity and temperature of the air among others. It has also proved difficult to develop pure theoretical relationships between the parameters because of the difficulty in determining the actual relationship between them. It is also understood that the forces holding the bound water in the matrix change with the parameters such that a small shift in one parameter might cause a completely different relationship (Saravacos, 1986). Therefore most of the existing relationships are either semi-theoretical or entirely empirical and although probably more than 100 such relationships have been developed only a few have received significant recognition (Menkov and Durakova, 2007; Menkov and Durakova, 2005; Štencl, 1999). Five of the more widely used relationships are the Chung -Pfof (Eq.3), Modified Hansley (Eq.4), Modified Oswin (Eq.5), Henderson (Eq.6) and the GAB equation (Eq.7) presented below.

$$RH = \exp \left[\frac{-C_1}{T + C_2} \exp(C_3 M_e) \right] \quad (3)$$

$$RH = \exp \left[-\exp(C_1 + C_2 T) M_e^{-C_3} \right] \quad (4)$$

$$M_e = (C_1 + C_2 T) \left(\frac{RH}{1 - RH} \right) \quad (5)$$

$$1 - RH = \exp \left[-C_1 T_{abs} M_e^{C_2} \right] \quad (6)$$

$$\begin{aligned}
 M_e &= \frac{C_1 C_2 C_3 RH}{(1 - C_2 RH)(1 - C_2 RH + C_2 C_3 RH)} \\
 C_2 &= C_4 \exp \left[\frac{C_5}{RT_{abs}} \right] \\
 C_3 &= C_6 \exp \left[\frac{C_7}{RT_{abs}} \right]
 \end{aligned} \tag{7}$$

Many researchers have also independently measured the equilibrium moisture contents (EMC's or M_e) of various food materials under varied conditions of environmental temperature and relative humidity. Some of these values are available in American society of agricultural and biological engineers (ASABE) year books while the constants of some of these models for selected products have also been published. Today, researchers are continuing with research for many other products in order to establish desorption and adsorption isotherms, the suitability of various EMC equations and heat of vapourization (Phomkong et al., 2006).

1.2. Product Composition Changes during Drying

The immediate and obvious effect of the reduction in water during drying of any product is a decrease in the gross weight of the product and an increase in the concentration of nutrients. In most cases the decrease in water content also makes the product more stable under normal storage conditions. However, undesirable changes in the chemical composition of the drying material may occur during the drying process leading to a final product that has low quality.

Slow rates of drying allow high respirations for long periods of time which in turn causes loss of carbohydrates (Desrosier, 1970). Other substances usually lost include carotene and vitamin C. Since materials also stay for extended periods of time at high moisture contents, the multiplication of bacteria and the development of yeast and molds may occur. Enzymatic reactions will also continue during the drying period unless certain pretreatments have been executed.

Fast drying accompanied by high temperatures on the other hand may cause chemical reactions resulting in a change in the content of heat sensitive material substances such as those responsible for flavour. Thiamin, ascorbic acid and carbohydrates (through millard reactions) may be lost if the right drying conditions are not employed (Clary, et al., 2007; UNIDO, 2007).

The importance of the heating temperature during drying has been known for many years. While working with rice at temperatures between 40 and 70°C Novosellov et al (1974) found that starch in the endosperm becomes pasty and partially changes to dextrin. The dextrin thus formed has a cementing action which reduces the number of cracks in the kernel and therefore increases the head-rice yield. Parboiling or wet heat treatment has a similar effect. The b-vitamin complex undergoes partial decomposing which results in its diffusion into the endosperm. Also, due to the formation of dextrin the head-rice yield of parboiled rice is higher and its increased hardness cause less breakage during milling. In recent years there has

also been extensive research in what is referred to as the glass transition temperature. The glass transition temperature is the temperature at which transition occurs from a hard, solid and amorphous state to soft, rubbery liquid state due to the increase in temperature of the material beyond a particular limit (Sundaram, et al., 2004).

It has been found that tens of thousands of compounds may be associated with the aroma or flavour of many foodstuffs (UNIDO, 2007; Farah and Donangelo, 2006). Although these compounds are to be found in minute quantities, the presence of these small quantities in the finished product is essential. At high drying temperatures the aromatic compounds may be lost due to chemical conversion of the original compound or due to the change of a volatile compound into the gaseous state which then escapes into the drying media.

The chemistry of the aromatic compound even for the most common foods is not well understood. The quality of many industrial products such as powder milk, instant coffee, tea and free flowing flours has been closely related to their aroma and flavour. Since these products are prepared by rapidly drying liquid solutions using high temperature air, the compounds associated with aroma and flavour may be lost through complex thermal degradation reactions that occur and due to the high volatility of some aromatic compounds (Karel, 1987).

1.3. Change in Physical Properties

The physical properties include length, width, surface area, volume, surface roughness, density, hardness, colour etc. Although not all the physical properties change during drying most of them are affected by the removal of water (Chua, 2006; Mwithiga and Jindal, 2003; Jia, 2002; Karuruzzan, 1992; Muthukumarappan et al., 1992; Sahu, 1989).

The rate of moisture removal in particular can be related to the development of cracks in grains. For a particle undergoing rapid drying the layer of material near the surface dries faster than subsequent layers further away from the surface. This causes a moisture gradient to develop across the particle which in turn introduces internal forces due to resulting differential shrinkage (Puitsin, 1953). Layers close to the surface tend to shrink more because of faster drying rates and to relieve the tensional forces created, cracks are formed.

Crack formation during drying depends on the rate of drying, size and the geometry of the particle. Large particles will develop larger cracks due to higher forces. Irregular shaped particles might not develop cracks especially if they are winkled because a change in volume has little effect on the surface area. This means that the magnitude of stress developed may not be sufficient to develop fissures.

In the preparation of certain products the drying conditions have to be modeled to achieve the desired preset bulk density and shape of finished products. This is especially important in baby foods and many other instant beverages where customer appeal and convenience during consumption demands it.

1.4. Seed Germination Potential

Seeds are biological systems whose germination potential must be preserved at all stages of the production. The seeds are normally to be stored for the period between harvest and the

next planting and this necessitates drying. The germination potential of a seed is susceptible to drying injury and can be related to the following factors;

- a) grain temperature during drying
- b) rate of evaporation of water from grain, and
- c) overdrying of the kernel

Sosulnikova and Shampanova (1970) while drying wheat seeds in tower and rotary dryers found that the temperature of the embryo was on average higher than the mean grain temperature. They found that if the grain was in constant contact with a hot surface at 120°C the viability was reduced by 45% in 30 seconds. The viability was reduced by only 16% if the seed was intermittently in contact with the hot surface. This is an indication of the relationship between drying temperature and viability.

The rate of moisture removal also related to the development of stress cracks. The higher the evaporation rate the higher the likelihood of stress cracks which in turn make the seed more susceptible to insect attack and mechanical damage during subsequent operations. Ptitsin (1953) found that the rate of moisture removal from wheat seeds could be increased to a maximum of 8% per hour without any adverse effect on the seed.

Over-drying apart from increasing drying costs also increases the possibility of mechanical damage of seed and should therefore be avoided. Development of cracks in seeds could also occur due to the adsorption tendency of over-dried seeds.

2. Dryer Performance

2.1. Drying

Moisture may be removed from a substance either by the application of heat or pressure. The most common however is the application of heat and the resulting process is called drying. The product being dried may be gas, liquid or solid.

Although there are many reasons for drying a substance the most common are to improve the keeping quality, ease handling and reduce freight costs. For foodstuffs preservation is by far the most important and drying should normally be carried within a stipulated period of time if deterioration is to be avoided.

Many methods of supplying heat to the product have evolved with modern technology.

In the most common dryers, heat transfer can be by convection, conduction, radiation or dielectric (Keey, 1972).

2.2. Dryer Type and Operation

Classification of dryers is difficult because of many variations in design. There exist differences in the operations of many dryers and also in the materials they are designed to handle. An extensive classification system of the different types of industrial dryers is given by Nonhebel and Moss (1971), however most designs are based on the following factors although the list is hardly exhaustive;

- a) Characteristics of the material
- b) Method of operation of the dryer
- c) Method of heat transfer, and
- d) Scale of operation

The operation of the dryer and indeed the control of the drying process depend very much on the temperature of the medium used to dry the product. Two distinct classes of dryer based on the temperature are recognized as high temperature dryers and low temperature dryers. The low temperature (near ambient) dryer is defined as one that uses unheated ambient air or air whose temperature is raised by less than 5°C to dry the product (Nellist, 1988). The drying period may range from 5 to 30 days and the product is dried in batches. In contrast high temperature drying systems work at temperatures of 40°C and above with air of low relative humidity. Drying takes a few hours to complete. These dryers can further be divided into stationary, cross flow, concurrent flow or counter current flow dryers based on the flow of both materials and air.

2.3. Modeling the Drying Process

Drying is a process in which heat and moisture are simultaneously transferred. A steady-state rate of transfer is normally not experienced since most materials dry entirely in the falling rate period. In most cases the laws of physics cannot be used to model the drying process due to the changing characteristics of the drying materials. Agricultural materials do not have standard shape and uniform size (particulate materials) and nor do they have a homogeneous composition.

To develop models based on scientific theory researchers have had to make numerous assumptions and approximations in order to overcome some of the barriers. Others have developed empirical models using statistical approaches. Each model can only be used for the specific product and drying conditions for which it was developed. These conditions include temperature, relative humidity, moisture content and air flow rates and any model will only work well within the specified range at which it was developed although tests can be carried out to determine the possibility of its extrapolation.

Many drying models that are based on coupled heat and mass transfer, mass transfer alone or heat transfer alone during drying have been developed. However, models that are based on changes in product quality are few (Nellist, 1986). Some common models are discussed below.

2.3.1. Single Particle Drying

Although dryers will normally hold large quantities of drying materials moisture has to be evaporated from each individual particle separately before being driven out of the bulk mass of particles. For this reason it is important to understand the kinetics of moisture removal from a single particle.

The complicated movement of moisture from the interior to the surface of a particle was explained by Luikov (Luikov, 1966). This movement which can be due to the three driving

forces of moisture gradient, temperature gradient or pressure difference is represented by the Luikov partial differential equations, Eq. 8-10.

$$\frac{\partial M}{\partial t} = \nabla^2 K_{11} M + \nabla^2 K_{12} T + \nabla^2 K_{13} P \quad (8)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{21} M + \nabla^2 K_{22} T + \nabla^2 K_{23} P \quad (9)$$

$$\frac{\partial P}{\partial t} = \nabla^2 K_{32} M + \nabla^2 K_{32} T + \nabla^2 K_{33} P \quad (10)$$

The pressure gradient in a drying particle is very small under normal drying conditions and this makes it safe to drop Eq. 10 as well as the pressure terms in both Eq. 8 and 9. Also most researchers have considered the coupling effect represented by the coupling constants K_{21} and K_{12} as minor therefore reducing Luikov equations to Eq. 11 and Eq. 12. The first equation (Eq.11) is synonymous with diffusion equation also called Fick's equation while Eq.12 is synonymous with the widely used heat equation. For the movement of moisture or temperature in the three dimensions of a solid object Eq.11 and Eq.12 can be expanded into the form of Eq.13 and 14.

$$\frac{\partial M}{\partial t} = \nabla^2 K_{11} M \quad (11)$$

$$\frac{\partial T}{\partial t} = \nabla^2 K_{22} T \quad (12)$$

$$\frac{\partial M}{\partial t} = D \left(\frac{\partial^2 M}{\partial x^2} + \frac{\partial^2 M}{\partial y^2} + \frac{\partial^2 M}{\partial z^2} \right) \quad (13)$$

$$\rho_g c_g \frac{\partial T}{\partial t} = \kappa \left(\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} + \frac{\partial^2 T}{\partial z^2} \right) \quad (14)$$

These simultaneous equations are usually solved numerically due to the difficulty of obtaining an analytical solution. Both the moisture content and the temperature within the particle are changing with both time and location. The rate at which both the moisture content and temperature are changing during the drying process is at the same time dependent on D, κ, ρ_g, c_g which are properties of the drying material and yet these properties are themselves changing with both temperature and moisture content.

At the particle surface there is continuous exchange of heat and moisture between the particle and the surrounding medium. The rate of transfer can be represented by Eq.15 and 16. In both equations the mass transfer coefficient and the heat transfer coefficient vary with

change in the medium properties such as relative humidity and air velocity. The equilibrium moisture content which is dependent on both the properties of the surrounding medium and the product itself can be represented by a suitable equation such as Eq.3-7. The initial temperature and moisture content of the particle must be known in order to provide the starting point of the numerical computation (Jia et al., 2002).

$$D \frac{\partial M}{\partial n} = h_m (M - M_e) \quad (15)$$

$$\kappa \frac{\partial T}{\partial n} = h_t (T - T_a) \quad (16)$$

The numerical computation method is complicated and requires a computer program that can repeat iterations that estimate moisture content and temperature. Usually the cross section of the particle has to be divided into sections so that the temperature and Moisture content at pre-selected equally spaced points (or nodes) can be computed after given short time intervals (Δt). There are many approaches to the solution and varied assumptions. Considerable computation time is required to produce predictive models and this depends on the number of nodes and the time steps used.

The biggest disadvantage to this approach is the fact that the relationships relating product and medium properties to moisture content and temperature should already be known. A different and independent research normally has to be done to develop each one of these relationships. Where a suitable equation for even one of the properties is not known then this approach cannot be used (jia et al., 2002).

Mass Transfer Models

Knowledge based mass transfer models are developed using Fick's law of diffusion. By assuming spherical coordinates (most agricultural materials approach the spherical shape as compared to the brick or cylinder standard shape) Eq.13 can be solved to give Eq.17 representing the removal of moisture at a given temperature of the drying air. Similar solutions for slabs like materials or cylindrical materials are represented in Eq.18 and 19. The moisture content of the particle in Eq.17 in this case is the average value and there is no consideration of the moisture gradient within the particle. The Variable X of Eq.17-19 is expanded into Eq.20 and is dependent on the shape of particle, moisture diffusivity and the drying time.

$$MR = \frac{M - M_e}{M_o - M_e} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \left(\frac{1}{n^2} \right) \exp\left(-\frac{n^2 \pi^2}{9} X^2\right) \quad (17)$$

$$MR = \frac{M_i - M_e}{M_o - M_e} = \sum_{n=1}^{\infty} \frac{4}{\lambda_n^2} \exp\left(-\frac{\lambda_n^2}{4} X^2\right) \quad (18)$$

$$MR = \frac{M_i - M_e}{M_o - M_e} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left(-\frac{(2n+1)^2 \pi^2}{4} X^2\right) \quad (19)$$

$$X^2 = \left(\frac{A}{V}\right)^2 Dt \quad (20)$$

The diffusion coefficient of the above equation varies with the temperature and relative humidity of the drying air. It may also vary with the moisture content of the product as drying proceeds. Many models however ignore the variation of this constant with change in moisture content and assume a constant value thus reducing their accuracy in predicting the drying process.

Other problems are encountered in the selection of boundary conditions. A common assumption is that the particle has uniform moisture content initially (M_0) and that at any other time after drying has started the surface moisture content is equal to the equilibrium moisture content (M_e) of the drying product for given relative humidity and temperature of the surrounding air (Eq.3-7). It is therefore indirectly assumed that the surface moisture instantaneously drops from M_0 to M_e and yet this is not practically possible (Thompson et al., 1968).

When the length of drying is sufficiently long it has been established that using only the first term of the series in Eq.17 18 or 19 can be acceptable. This (in the case of Eq.17) yields Eq.21 which has results that are more than 95% accurate provided that the diffusion constant, D falls between .22 and 1. By combining the terms in the exponent into a single drying constant Eq.21 becomes Eq.22 which is also referred to as the Henderson and Pabis model.

$$MR = \frac{6}{\pi^2} \exp\left(-\frac{\pi^2}{9} \left(\frac{A}{V}\right)^2 Dt\right) \quad (21)$$

$$MR = A \exp(-Kt) \quad (22)$$

Apart from ignoring the fact that the diffusion constant changes with moisture, Eq.22 also usually ignores the fact that shrinkage occurs during drying and that this may lead to a change in the ratio of surface area to volume. However, despite these shortcomings this simplification has enabled the development of semi-theoretical equations that are based on the first term of the series solution of Eq.13. Some of the semi-theoretical models (equations) are the most widely used models to represent the drying of porous materials today (Jamradloedluk, et al., 2005). Other widely used thin layer drying models other than the Henderson and Pabis model are the Newton (Eq.23), Page (Eq.24) and the Modified page model (Eq.25) and these are presented below.

$$MR = \exp(-Kt) \quad (23)$$

$$MR = \exp(-Kt^n) \quad (24)$$

$$MR = \exp[-(Kt)^n] \quad (25)$$

In order to get more accurate predictions of moisture content during drying some researchers have taken in to considerations the variation of the diffusion constant with moisture. Bruce (1986) developed a drying model for barley based on the Ficks diffusion equation. Diffusion was related to moisture using an exponential function. He also made an assumption that the surface moisture of the particles approached the equilibrium moisture content at a rate proportional to the air temperature. The computation time required when using this approach was more when compared to that required when using Eq.22-25 although it gave more accurate predictions.

Empirical thin layer drying equations have been developed by several researchers (Broker et al, 1974; Thompson et al., 1968). One of the older empirical models is Eq.26 also popularly known as Thompson equation. It was originally developed for shelled corn but has been widely adapted and used to predict the drying of other products (rice Steffe and Singh, 1980; navy beans and sunflower, Radajewski et al., 1992; Syarief et al., 1984) over the years and it continues to attract attention even today (Waewsak et al., 2006). The Wang and Singh model presented in form of Eq.27 has also received reasonable attention.

Empirical models tend to predict the drying behaviour more accurately for small ranges of drying conditions while still being easier to develop when compared to the semi-empirical model. It is for this reasons that they are likely to continue being widely used in the future even when they are lacking in theoretical basis.

$$t = A \ln(MR) + B [\ln(MR)]^2 \quad (26)$$

$$MR = 1 + At + bt^2 \quad (27)$$

Heat Transfer Models

Heat transfer in a dryer is usually either by convection or conduction. Transfer by radiation is minimal and is usually ignored. In solar dryers however, heat transfer radiation dominates. When the equation for convective heat transfer between the particles and the sounding medium is used a uniform particle temperature throughout the drying period is normally assumed. This however is an oversimplification of the situation since the temperature inside a particle varies with time and locations and is therefore not uniform. A more accurately approach is to use the heat conduction drying model or the lumped model. The basic problem in the solution of all heat transfer equations however lies in the determination of the surface heat transfer coefficient. Many empirical equations have been suggested and all give different solutions (Bruce, 1985, Toledo, 2007, Sokhansanj and Bruce, 1987). The choice of the appropriate equation to use lies with the individual and depends on the drying conditions such as the airflow rate, air temperature and humidity as well as the predominant type of energy transfer.

2.3.2. Deep-bed Drying Models

Models for the drying of materials in deep beds differ significantly from single layer drying. The properties of the medium (usually air) surrounding fully exposed particles under single or thin layer drying normally remain fairly constant throughout the drying period. However, in

deep-bed drying and other dryers where the product is in motion during drying the properties of the product and the properties of the surrounding air are changing with location and time.

We can model the drying in a deep bed by treating the deep bed as a system of many thin layers or elemental volumes of drying material one piled on top of the other. The materials in each of the elemental volumes can remain stationary throughout the drying period (batch dryers) or it can change location with time during drying such as in continuous flow dryers. We also recognize that where the air is forced through the drying materials, the exit properties of air leaving one layer will become the inlet properties for the next layer. Similar argument can be advanced for the next layer through which the air passes and for all other subsequent layers until the air exits from the dryer.

We must produce a mass and energy balance for both the product and the air passing through the control volume in a given unit of time. In essence the mass gained by the air in form of vapour is equal to the mass lost by the product. Also there should not be any net gain or loss of energy for both air and control volume even after the air passes through the elemental volume and carries away the moisture.

In order to simplify the solution of simultaneous equation of the complicated heat and mass transfer problem in the control volume researcher usually make a number of assumptions and it is common to assume a one dimensional problem. While the assumption listed below have been used under a variety of situations, it is important to select the ones which are likely to be valid for the particular situation (Fortes and Ferreira, 2004; Lacerda et al., 2004; Sarisvastava and John, 2001; Brooker et al., 1974).

1. Drying air is an ideal gas mixture
2. Bin walls are adiabatic with negligible heat capacity
3. Product volumetric contraction and expansion are negligible
4. Heat transfer among particles is negligible
5. Particles are impermeable to the drying air
6. Particles are uniformly distributed inside the dryer, mix uniformly with air and behave as water sources and sinks
7. Steady state is achieved within the control volume
8. air and/or solids flow in one direction
9. Internal diffusion is the predominant mechanism of moisture transfer
10. Convection is the predominant mechanism of heat transfer
11. Heat losses are negligible
12. Solid flow is uniform and air velocity is flat
13. For the control volume change in product moisture and temperature with time is negligible when compared to their change with location (OR change in air humidity and temperature with time is negligible when compared to their change with location)
14. Specific heat capacities of both air and product are constant over short time periods
15. An accurate thin layer drying equation and equilibrium moisture isotherm for the material is known

An assumption that there is negligible change in volume although reasonable for small drying ranges might not be justified where there is a large change in moisture during drying such as in the drying of fruits and vegetables. Under such circumstances it might be important

to determine the variation of volume with moisture since this will in turn affect other variables such as air flow profile and velocity through the dryer (assumption 12).

Also the assumption that steady state is achieved within the control volume (assumption 7) and change in moisture and temperature with time is negligible when compared to their change with location (assumption 13) cannot be valid in batch dryers. This situation can only be achieved in continuous dryers where a situation pertains such that the product entering the control volume is always at the same temperature and moisture content, the air entering the control volume is also at same humidity and temperature and that the exit conditions of both product and air remain constant over time. While this is achievable in a continuous dryer, the dryer will still need considerable time from the time of startup for this equilibrium to be reached. The moisture content of the product at the entry point will also have to remain fairly constant in order to avoid upsetting the equilibrium.

For any dryer and after making the right assumptions we normally have to solve four simultaneous equations for four variables which are temperature of air, temperature of product, specific humidity of air and moisture content of product. Each one of the four properties will also be changing either with location or with time or with both location and time as the drying proceeds.

Static Bed Modeling

Consider the control volume inside the static bed dryer as shown in Fig.5. The air is passing through the control volume at a steady rate through the cross section area S . For a small time interval we can write the moisture mass balance as Eq.28. The mass of vapour evaporated from the product is equal to mass of vapour removed from the control volume plus the vapour in the air that remains in the void space of the control volume.

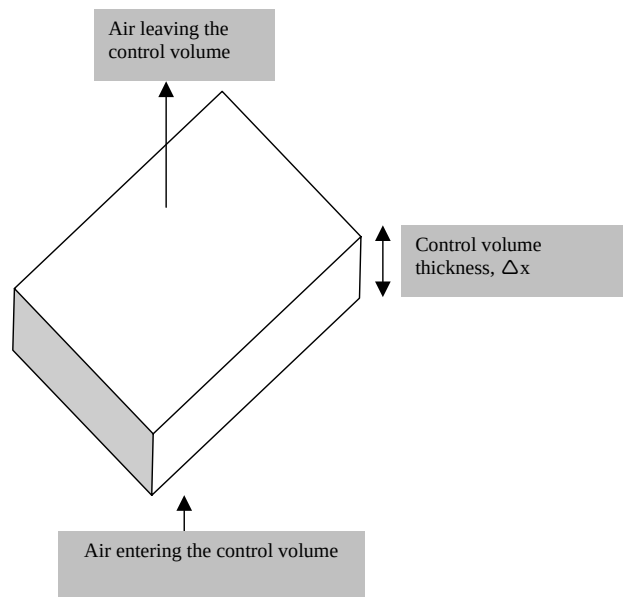


Figure 5. Elemental product layer of surface area, S and thickness, Δx through which the drying air passes at a uniform velocity, u .

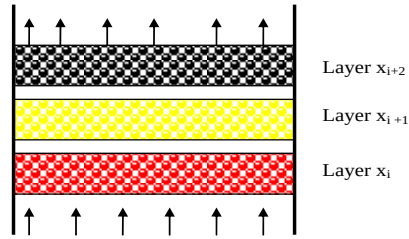


Figure 6. A cross-sections of a static bed dryer showing horizontal layers of product of thickness dx each through which the drying air is passing.

$$\rho_g \frac{\partial M}{\partial t} = G \frac{\partial W}{\partial X} + \varepsilon \rho_a \frac{\partial W}{\partial t} \quad (28)$$

The difference in enthalpy of air coming in and air going out of the control volume can be presented by the left-hand side of Eq.29. This is equal the increase in the sensible heat of evaporated water minus convective heat transfer to the product and less the sensible heat increase in the air trapped in the control volume.

$$G(C_a + C_v W) \frac{\partial T}{\partial X} = \rho_a C_v (T - \theta) \frac{\partial M}{\partial t} - h_a (T - \theta) - \rho_a \varepsilon (C_a + C_v W) \frac{\partial T}{\partial t} \quad (29)$$

The change in the energy in the product is represented by the left-hand side of Eq.30 which must also be equal to the sum of energy transferred to the product through the surface and the energy for the change of state of evaporated water.

$$\rho_g (C_g + C_w M) \frac{\partial \theta}{\partial t} = h_a (T - \theta) + h_{fg} \frac{\partial M}{\partial t} \rho_g \quad (30)$$

If we further assume that the change of air humidity with time ($\frac{\partial W}{\partial t}$) and the change of air temperature with time ($\frac{\partial T}{\partial t}$) within the control volume is negligible for small time intervals then Eqs.28-30 can be modified into Eqs.31-33.

$$G \frac{\partial W}{\partial X} = \frac{\rho_g}{G} \frac{\partial T}{\partial t} \quad (31)$$

$$\frac{\partial T}{\partial X} = \frac{1}{G(C_a + C_v W)} [\rho_a C_v (T - \theta) \frac{\partial M}{\partial t} - h_a (T - \theta)] \quad (32)$$

$$\frac{\partial \theta}{\partial t} = \frac{1}{\rho_g (C_g + C_w M)} [h_a (T - \theta) + h_{fg} \frac{\partial M}{\partial t} \rho_g] \quad (33)$$

These three equations (Eqs.31-33) contain four unknown variables which are $\partial T(x,t)$, $\partial \theta(x,t)$, $\partial W(x,t)$ and $\partial M(x,t)$ at any location and any time. In order to solve for these variables simultaneously we need one more equation. A suitable thin layer drying equation such as Eq.34 can be used to determine the rate of moisture removal with time. The drying rate constant of the selected thin layer drying equation is dependent only on humidity, air temperature and type of product.

$$\frac{\partial M}{\partial T} = -K(M - M_e) \quad (34)$$

As shown in Fig.6 however, a batch dryer can be assumed to be made up of several thin layers placed one on top of the other. The drying air passes from one layer to the next as it trespasses through the dryer. As the air passes through the layers its temperature and humidity changes as heat is transferred to the product and moisture evaporated into the air. These changes are represented in the four simultaneous equations (Eq.31-34) ensuring that there is both an energy and mass balance.

There exist quite a number of ways of solving the four simultaneous equations. If we know the properties of air that is entering the x_i layer we can calculate all the four unknowns after a short drying period (at time $t + \partial t$) by simultaneously solving the four equations. The solution can then be used to determine the exit air temperature and humidity which will in turn become the entry properties of air entering the next layer (x_{i+1}) for the same drying time interval of between t and $t + \partial t$. By repeating the solution procedure and extending it to each successive layer the product and air properties at every position in the dryer for the time interval t to $t + \partial t$ can be determined.

The solutions of the four simultaneous equations at the x_i layer can also be used to find new moisture content and product temperature at the end of drying time $t + \partial t$ in each layer. These values of product temperature and moisture content together with the properties of air entering the layer can be used to solve the simultaneous equations for the next time interval of $(t + \partial t)$ to $(t + 2\partial t)$. In this way the progressive change in the variables with time can be computed.

Simplified Solution

An example of a simplified calculation method is presented for a single layer of known location. If the air temperature and humidity at the point of entry into the layer and both the product temperature and moisture content at the beginning of the short drying period are known then the moisture content at time $t + \partial t$ can be given in form of Eq.35(Mandas and Habte, 2002).

$$M_i^{t+\partial t} = M_i^t + \left(\frac{\partial M}{\partial t} \right) dt \quad (35)$$

In order solve this equation we have first to estimate the rate of change of moisture content (or rate of evaporation) with time. However this rate also changes with time because the value of the drying rate constant is dependent on air temperature and humidity at this location and these two are also changing with time. We therefore need to find an average rate for the period of t to $(t + \partial t)$.

In the first estimate we assume that the rate of drying is dependent on the properties of air at time t and can therefore be presented in the form of Eq.36. The solution of Eq.36 for $(\frac{\partial M}{\partial t})$ when inserted into Eq.35 allows us to calculate the estimated moisture content at the end of the drying period. However, Eq.35 at this stage tends to exaggerate the rate of drying and therefore gives a moisture content that is much lower than the actual value.

$$\left(\frac{\partial M}{\partial t} \right)_i^{t+\partial t} dt = K \left(M_i^t - M_e \right)_i^t \quad (36)$$

In order to correct the problem of over estimating the rate of drying we need to find the average drying rate during the period t to $(t + \Delta t)$ using the following procedure. We compute the rate of change of air temperature with location (Eq.32) and the rate of change of product temperature with time (Eq.33) and this is done by replacing the term $(\frac{\partial M}{\partial t})$ in each of these equations with the average solution obtained from both Eq.36. This in turn allows us to calculate the product temperature at the end of the drying period $(t + \Delta t)$ and the temperature of air the point of exiting the layer x_i . Both the air exit temperature and the grain temperature at time $(t + \Delta t)$ can be used to find another drying rate constant and rate of drying at time $(t + \Delta t)$ as given in Eq.37. The average drying rate constant is then computed using Eq.38 and this average value is finally inserted into Eq.35 in order to compute the final moisture content of the layer at $(t + \Delta t)$.

$$\left(\frac{\partial M}{\partial t} \right)_i^{t+\partial t} dt = -K \Big|_i^{t+\partial t} \left(M \Big|_i^{t+\partial t} - M_e \Big|_i^{t+\partial t} \right) \quad (37)$$

$$\left(\frac{\partial M}{\partial t} \right)_{average} = \frac{1}{2} \left(\left(\frac{\partial M}{\partial t} \right)_i^t + \left(\frac{\partial M}{\partial t} \right)_i^{t+\partial t} \right) \quad (38)$$

Following the above solution the adjusted values can then be used to compute the new value of product moisture and temperature at the end of the time step and also the exit value of air temperature and humidity using Eq.31-33. For the next time step the whole process of computation starting with Eq.36 has to be repeated.

Moving Bed Modeling

Sometimes we need to model the drying of a moving product as is the case in con-current and counter current cross flow dryers. Under these conditions the same four equations (Eq.31-34) that were used for modeling the batch dryer can be used with only a small modification.

In the case of the static dryer we used a control volume which had a volume equal to one unit in order to produce the four simultaneous equations for mass and heat transfer. The mass of product in the control volume can also be given by Eq.39. Clearly, the density values (ρ_g) appearing in both Eq.31 and Eq.33 represent the mass of material in the control volume. In the case where the material is flowing through the control volume the density values in the two equations (Eq.31 and 33) need to be replaced by the actual mass of product (G_p) that is flowing through the control volume

$$Mass = Volume \times Density = 1 \times \rho_g = G_p \quad (39)$$

There is another main difference between batch and continuous dryer modeling. While as the material in a batch dryer remains at the same position during drying so that product properties at the end of each time step become the initial product properties for the next time step this is not the case for continuous dryers. The material in a particular layer during a given time step will have moved to another layer by the end of the time step and its location will depend on the direction of motion and the flow-rate. The flow-rate and direction of flow must be taken into consideration when computing values of the variables during the next time step or the next layer.

2.4. Quality Model

The nature of the change in product quality in a low temperature dryer differs from that of a high temperature dryer. In a low temperature dryer spoilage occurs due to slow removal of moisture and the provision of temperatures which are suitable for the multiplication of microorganisms. Quality loss is therefore caused by microorganisms and respiration. The reverse is true for high temperature dryers. The rapid removal of moisture and rise in temperature inactivates enzymes and kills most of the micro-organisms. The rise in temperature however also causes other undesirable changes resulting in thermal damage and quality loss.

To put a quantitative measure on the loss caused by drying conditions however is difficult and cannot be generalized since it depends very much on the end use of the drying product. The quality of the product can therefore be measured using several different scales.

2.4.1. Quality of Animal Feeds

The quality of animal feeds can be based on the availability of protein lysine. Nellist (1987) suggested 10% as the highest acceptable drying lysine loss for animal feeds. This conclusion was reached after comparing the results of several other researchers and finding that a loss which fell beyond the 90% lysine content was always considered unacceptable. Mathematical models for thermal degradation of lysine are yet to be developed.

2.4.2. Seed Quality

Thermal damage of seed grains is reflected in germination tests. Early researcher found that the temperature and moisture content can be related to quality loss (Ptitsin, 1953, Corrêa et al., 1999; Sutherland and Ghaly, 1982). When a grain at fixed moisture content is held at a fixed temperature of heating medium for some extended period of time, there exist a critical temperature at which the viability of the grain will start falling. Below this temperature no viability loss is noticed irrespective of how long you hold the grain (Nellist, 1988). If the values of the critical temperature and the moisture content were each varied separately while holding the other constant its is found that the time required before viability starts to fall decreases with increase in moisture content and also decreases with increase in temperature (Nellist and Bruce, 1987). This relationship can be presented graphical in what is called Probit's viability. Relationships which show the conditions which ought not to be exceeded in order to limit viability loss to a fixed amount can also be produced in a similar manner.

2.4.3. Flour Quality

Flour quality as related to milling and pasting characteristics, loaf volume and dough handling properties can be shown to follow a trend similar to that of seed viability (Yadav et al., 2006; Haros and Suarez, 1997; Ghaly et al., 1973). The research work of Nadel et al (2002) which reports a significant reduction in energy requirement during grinding if wheat is microwave dried prior to grinding is worth mentioning. However, there have been limited attempts to develop mathematical models that relate the baking qualities or specifically change in loaf volume to drying temperature and moisture content changes (Bruce, 1992; Becker and Sallans, 1961).

2.4.4. Mold Development Model

The development of molds is particularly important in low temperature dryers. Nellist (1988) studied mold development in barley and rape. He measured the length of time that each product could stay without developing any visible molds at a given drying temperature, relative humidity and moisture content. Other studies related to mold development have also been carried by Bruin and Luyben (1980). However there has been limited research activity towards the development of models for predicting the growth of molds during drying.

2.4.5. Other Quality Models

The changes occurring during drying and specifically those that related to product quality are many and the importance of the changes varies with the product as already explained. There have been studies on variations of colour during drying (Jamradloedluk et al., 2005; Mwithiga and Jindal, 2004) hardness (Jamradloedluk et al., 2005) microstructure (Jamradloedluk et al., 2005; Askari et al., 2006). The development of models for predicting these changes is complicated due the wide variations in product composition and drying conditions. Therefore , there is still a lot of work that can be done in this area of research especially with products whose quality is highly dependent on the aromatic substances that they contain.

2.5. Optimization of the Drying Operation

The broad optimization objective is the maximization of quality and minimization of drying costs. This objective is in line with consumer behaviour and preference because people in general prefer to buy goods that have the highest possible quality while paying the least possible price. Due to the fact that there are many dryer designs and just as many ways of operating them, there are many variables and operating procedures that can be used in trying to reach the optimization objective. In some cases other minor objective functions have to be set within the main objective function. Bruin and Luyben (1980) listed many end results that might be desired in a drying operation. But then, there are just as many if not more ways of trying to achieve the desired result. Where as many alternatives as possible are to be considered it is sometimes necessary to carry out many experiments or simulations (where models are available) in-order to eliminate some non feasible alternatives. In most cases formal optimum seeking methods cannot be used (Islam et al., 2004; Houben et al., 2004; Keey, 1971).

An ideal objective function would include both the quality and economic aspects of drying. While the drying costs can be calculated with good accuracy, measurement of quality is difficult. The ultimate authority on quality of a product is the consumer, and yet the product might pass through other industrial processes which also affect its quality before reaching the consumer. Even when the dry product goes directly to the consumer, use of consumer preference should be avoided as much as possible because it is too expensive and keeps on changing with time. The cost of measuring consumer preference might offset the gains in sales on the long run (Bruin and Luyben, 1980). It is therefore more desirable that quality be described by mathematical models (which are based on physical laws) relating quality directly to the drying conditions. Where one or more quality factors are to be considered, a weighted average of all factors should be a good indicator of quality. In most cases however one or two factors dominate as the perceived quality indicators and it is therefore not necessary to consider the other quality factors (Soares et al, 2004).

Objective Function Based on Cost of Drying

The cost of drying is reflected in the Specific energy consumption (SEC) which is defined as the average energy required to evaporate one unit of water. The SEC is a function of the design of the dryer, the drying conditions and of the material being dried.

The approach to the determination of SEC is to add up all energy inputs during drying and then divide the sum by the amount of water removed. Energy inputs may vary from one dryer to another but should normally include heat energy, energy used to drive the fan and any other conveying components and labour inputs. Where the relationship between the energy and cost can be determined accurately, the specific cost of drying can be computed. This approach is good at selecting a dryer based simply on how much energy will be required to remove a unit of water during drying. It has short comings in that it does not take in to consideration the fact that the dryer or drying condition that leads to the lowest costs might not necessarily produce a product with the highest quality or returns. On the other hand the lowest SEC in most cases does not lead to the highest capacity and yet capacity has a direct bearing on operational profits.

In order to make reasonable business decisions it is necessary to find a way of considering the amount of energy used during drying and also to quantify the quality losses or gains as affected by the drying process. This can be done by put a monetary value on both energy and quality. A good example where this can be done is in such cases as in over-drying. Apart from increasing drying cost because of using more energy and reducing the final mass of the product that could have been sold if the product was dried to the right moisture content, over-drying might also lower quality through increase in thermal stresses. The increase in thermal stress and hence lowering of quality can be converted into monetary terms and added to the total cost of drying.

Most optimization strategies are based on cost analysis without considering quality mainly due to the difficulties encountered in the measurement and monetary quantification of quality (Rodriguez-Jimenes et al, 2005). Where quality is considered, it is only used to set boundary conditions (spoilage or damage levels) within which the cost function is contained (Soares et al, 2004).

Several strategies can be used to try and lower the SEC as outlined below;

- a) Selection of a dryer which has low SEC,
- b) Lowering of initial moisture content of material entering the dryer,
- c) Air recirculation,
- d) Product preheating,
- e) Dryer staging (varying drying air conditions in stages as drying proceeds,
- f) Product tempering and,
- g) Proper choice of inlet temperature.

Soares et al., (2004) approached the optimization problem of low temperature dryers by first setting a time limit within which drying should be accomplished and also setting a maximum acceptable deterioration of quality for the product. They then set about to minimize energy consumption within these two limits by varying a set of operational factors such as initial moisture, dryer capacity and diameter, loading rate, and fan type and rating. They concluded that it was possible to optimize the performance through these management strategies.

Ryniec and Nellist (1991a and 1991b) studied the drying of wheat at near ambient temperature conditions by setting two objectives. They wanted to minimize the drying cost and avoid the problem of over-drying. They used two control methods; they could vary the air flow using a fan at three levels and change the heater input at 10 levels. The STOREDRY simulation program was used to simulate drying for various combinations of air flow and heat inputs using 20 years weather data. They found that compared to the conventional method of running the fan throughout the drying period without supplemental heating, some of their various fan heater combinations could save up to 34% in energy cost during fair weather.

Mittal et al. (1984) employed a dryer staging strategy where corn was dried from 22% to 18% by operating a fan continuously and then from 18 to 15.5% by operating the fan intermittently. They reported a 5-31 % saving on energy when compared to uncontrolled low temperature drying in favourable years.

Brook and Bakker-Arkema (1980) studied the design of multi-stage dryers using computer optimization. The effect of air temperature, air flow and length of dryer on the cost of drying was determined. A breakage susceptibility model was included in their objective

function. They concluded that although the capital cost of a multistage dryer was higher than that of a one stage dryer their operational cost was significantly lower.

Other researchers who have studied the optimization of the drying operation include Bridges et al. (1980) who studied the optimization of drying depth for batch-in-bin corn drying and Barre and Hamdy (1974) who determined the optimum filling rates for in-storage drying.

All the above workers had different optimization strategies but generally the same objective function. Each one of them can therefore claim to have optimized drying but this would only be true for the particular drying conditions, the specific equipment that he used and the boundary conditions that he set for himself.

3. Dryer Control

Introduction

As more and more people become educated on their nutritive needs demands that manufacturers to produce high quality food products will increase. Improvement of the drying process which is one of the most common processes in the manufacturing of food and feeds is therefore an on going process. With the high demands on quality, control of the drying operation can no longer be left entirely to the dryer operator. The automatic control of dryers is in today's world absolutely necessary.

The main objective for installing controllers in a dryer is:

a) To act as safety gadgets

Electrical circuits are normally incorporated in the power circuit of various dryer components. These circuits act as monitors of abnormal events such as the tripping of a conveyor, blocking of the wet bin or the unloading auger, no air supply from the fan and burner failure. In the event of any of the above taking place, the controller either signals the operator and pin points the fault or/and automatically switches off the entire dryer until the fault is corrected.

b) To control the drying operation with the aim of reducing cost and quality loss

This can normally be achieved by measuring the inlet and outlet air temperatures and air relative humidity and/or the respective values of grain temperature and moisture content. These measurements are then used as a basis for controlling heat inputs such as the amount of fuel burned per unit time. In the case of a continuous dryer, air and product throughput can also be controlled.

This chapter concentrates on the control of the drying operation. Further information on safety aspects can be found in Brooker et al (1974) as well as in many other books on automatic control in industry.

The control of a drying operation is hinged on a desired output irrespective of the inputs. The desired final moisture content is normally fixed by the management. Any other desired result such as minimum acceptable quality, minimum length to dry, etc becomes secondary objective functions. The control action therefore involves three steps;

- a) Sensing a parameter that reflects the drying condition and which can be related to the desired result,
- b) Making a decision on the desired action which depends on the comparison of the measured parameter and the desired result,
- c) Acting to control any error (deviation) from the desired result

3.1. Sensors and Sensed Parameters

The four parameters which are normally sensed and monitored for the purpose of controlling the dryer are temperature, humidity, airflow and moisture content. These properties are measured either directly or indirectly using sensors placed at strategic locations in the dryer. Whatever the property being monitored the position of the sensor is very important since it relates to the accuracy of the measurement taken and to the ability of the controller to respond to the measured parameter (Ortega et al., 2007; Bakker-Arkema, 1990).

3.1.1. Temperature Sensing

The most common measured temperatures are;

- a) Dry and wet bulb air temperature at inlet and outlet, and
- b) Product surface or bulk temperature.

The dry and wet bulb air temperatures are indicators of the drying potential and can be used to make a decision on whether to increase or decrease the heat input. Another use of the dry and wet bulb temperature is to indirectly determine the relative humidity of the air.

The grain surface temperature is frequently used to determine the moisture content of grain in high temperature dryers since in most dryers the grain temperature increases as drying proceeds. The grain should be removed when its temperature corresponds to the desired final moisture content. This method of indirectly determining the moisture content is likely to fail when drying conditions keep on changing because the relationship between grain temperature and moisture content is not linear as often assumed. An even less accurate method used to determine the moisture content is measuring the exit air temperature and relating it to moisture content through a mathematical relationship. Where moisture sensors are not available or strict adherence to the set value is not necessary, temperature sensors present a cheap alternative and are therefore acceptable.

Three types of temperature sensors which are commercially available are thermocouples, resistance temperature detectors (RTD) and thermistors (Tong, 2001). Thermocouples are the obvious choice for dryers because they have a large range of operation and are adapted to remote sensing.

3.1.2. Humidity Sensing

Humidity is monitored in low temperature drying to avoid introducing very moist air which could wet the drying product. Another purpose of measuring the relative humidity is to control the final moisture content, M_{set} of the drying product. The lowest allowable relative

humidity is set equal to the equilibrium relative humidity (ERH) of M_{set} . The product can then be dried without any danger of overdrying. Humidity sensors are widely used in low temperature drying but they are not as common in high temperature drying.

Hygrothermal based humidity measuring instruments are commercially available and range from the widely used wet and dry bulb thermometer, dew point hygrometer, salt dew probes to hygrometric resistors and capacitors (Fuller and Charters, 1997; Harding, 1984; Keey, 1971). Most of these instruments need a clean environment to function accurately. Additional provisions such as clean water and adjusted air- flows for the wet and dry bulb thermometer or radiation shielding for the dew point (chilled millor) hygrometer may be necessary (Guo et al., 2004).

3.1.3. Air Flow Rates

Air flow signals may act as a warning that the dryer is running out of drying material. Under such circumstances a decrease in product depth is accompanied by an increase in air-flow. The controller can be set such that it cuts out fuel supply to the burner and switches of the fan if the airflow exceeds a set limit. The airflow can also be used as a measure of the drying rate since faster air-flows means higher drying rates.

Airflow sensing instruments range from the simple sail switch and diaphragm switch (Brooker et al., 1974) to the more complicated cup anemometer and paddle wheel anemometer. The suitability of air measuring instruments is judged on their ability to reproduce a measurement over a long period of time (no drifting tendency) and not particularly on their precision (Gates et al, 1991).

3.1.4. Moisture Content Sensing

In grain dryers the product supplied to a dryer over a day may vary in moisture content by as much as 15% (Bakker-Arkema, 1990). This grain has to be dried to the same moisture content and therefore requires almost constant variation of the residence time because it is fed into the dryer continuously. It is therefore almost impossible to maintain constant output moisture content no matter how accurately the moisture content inside the dryer is monitored.

This problem is due to the fact that a change in the discharge rate affects the product in every location inside the dryer and yet this effect is not corrected until the product reaches the discharge point (Bruce, 1986). Over shoots and undershoot of the required moisture content can therefore not be avoided.

The most common method of determining the moisture content is to measure the temperature and then calculate the moisture content using a predetermined mathematical relationship (Temple and Van Boxtel, 2000; Rodriguez et al., 1996); Keey, 1971). This method is likely to introduce some error because the relationship between moisture content and temperature is not linear and depends on many other factors. However the method has been widely used because temperature sensors are cheap and also due to lack of moisture sensors.

Commercially available moisture meters predict moisture on the basis of the dielectric property of a wet material. They require frequent calibration (twice a day at least) because they are affected by both temperature and bulk density. It is noted here that in any dryer the bulk density may changes with the rate of flow of material through the dryer and also due to

the resulting shrinkage as water is drawn from the material. If this sensor is to be used with a microcomputer based controller a recalibration subroutine need to be included in the software (Bruce and McFarlane, 1993; Whitefield, 1988b).

3.2. Control Decision

The decision of the control action is based on the management's objective criteria. One desired result is that the product exiting the dryer has constant final moisture content. The control action should therefore act in a way that will correct the discrepancy between the desired moisture content, M_{set} and the sensed moisture content, M_{sen} . The magnitude of the control action at time, t is therefore proportional to the magnitude of the difference, $(M_{\text{set}} - M_{\text{sen}})$, which is referred to as the error, $e(t)$ (Bakker-Arkema, 1990).

The signal received from the sensor is usually non linear and therefore need to be linearized if the right control action is to be taken. This requires the design of a control algorithm for each controller (Liu et al., 2006; Gates et al., 1991; Whitfield, 1988a; Nikolic and Mojsovski, 1986). A sensor linearizing circuit was developed by Stringam et al. (1989) who claim that the circuit can linearize the signal of any sensor provided the sensor calibration curve can be digitized and stored in memory. The circuit requires an A/D and a D/A convertor.

The control decision may be reached by making use of drying models to simulate drying and choose the optimal operating conditions. Under such circumstances many drying variables may be considered and a ready to use programme which is able to compute, compare and discard unsuitable alternative within reasonable time should be available. The hardware should also be able not only to receive sensor signals through a suitable input output port but also to send out a signal of the desired action.

3.3. The Controller

The action of the controller is to execute the decision once it receives a signal. Because of the nature of the control action desired low temperature drying controllers differ significantly from high temperature controller.

3.3.1. Low temperature Controller

Although in theory there can be unlimited control strategies, the components that can be manipulated in order to achieve the desired result are few. In full-bin control only the heater and the fan can be controlled by either changing heat input per unit time or the air flow rate. In layer drying the rate of filling the bin provides a third method of control. There are however many combination of fan and heater control strategies. Bakker-Arkema (1990) lists 21 low temperature drying control strategies for controlling fan and heater only.

The traditional method of running the fan continuous and without any supplemental heat until the desired moisture content is reached (conventional or uncontrolled drying) is normally considered as the bottom line. Any control strategy is therefore supposed to have a lower SEC when compared to the conventional drying. The function of the controller is

therefore to switch on and off the fan and/or heater at the appropriate moment (Islam et al., 2004; Fuller and Charters, 1997).

3.3.2. High Temperature Controllers

The drying rate in a high temperature dryer is many times faster than that for near-ambient drying conditions. The control strategies employed are therefore different and depend heavily on the manipulation of the flow rate of the product. Although the drying rate depends on the air flow rate, the drying air temperatures and grain flow rate, only the grain flow rate is available for controlling the drying process because it is expensive and complicated to vary the other two parameters (Nybrant, 1988). The controller action is to adjust the speed of the unloading auger as may be desired and to ensure that the outlet moisture content is as close as possible to the desired value (Arjona, et al., 2005; Temple, et al., 2000).

Controllers which depend on the sensing of the outlet moisture content have a time lag in their control action called the dead time. This delay is equal to the residence time or the time that the grain takes to travel from the inlet to the outlet. On the other hand however, controllers which depend on the sensing of the inlet moisture content can take immediate corrective action by predicting the required residence time.

3.4. Quality of Control

It should be possible to measure the success or failure of a control system by measuring its ability to maintain steady outlet moisture content and also maintaining consistency with the desired level. Manual control of a dryer often leads to significant deviation from the desired moisture content. Bakker-Arkema (1990) studied the operation of a cross flow dryer under both manual and automatic control. The experienced operator measured the inlet and outlet moisture content and then, based on his experience, changed the r.p.m. of the unloading auger. However the operator persistently overdried the grain by an average of 0.9% from the desired 14.5%. Douglas et al. (1992) compared the performance of manual control, temperature control and automatic control. The manual control managed to keep the outlet moisture within a narrow range of 18.72% to 21.35% while the average deviation of moisture from the required moisture was 0.41%. A temperature controller however was completely out of the required range of moisture content at the outlet (20%) and it had a wide band of outlet moisture contents. When an automatic controller was used however it managed to perform better than both manual and temperature control.

Controllers normally have to undergo more rigorous test to determine their robustness under extreme conditions (Whitfield, 1988b). These major tests include their ability to respond quickly to;

- a) Dryer start-ups under wet product loads,
- b) Sudden changes in input parameters such as inlet moisture content suddenly changing by 10%, and
- c) Change in residence time.

Automatic control of food drying is certainly economical and reliable when compared to manual control. However, more research in the development of sensors and control algorithms for continuous dryers has to be done. The development of suitable drying models for on-line decision making will also make a major contribution to dryer control.

4. Conclusion

The importance of dryer control cannot be overemphasized. Although advances have been made in the development of both controllers and sensors, the control of dryers is still far from perfect. There is therefore need to improve the accuracy and reliability of sensors especially in the sensing of moisture content. Control algorithms for the controllers also need to be developed using new techniques.

The future of optimization of the drying operation relies heavily on our ability to model and simulate the process. With the increase of availability of microprocessor technology, modeling and simulation has become relatively easy and can be handled with speed and accuracy. The number of test needed to optimize a drying operation can therefore be considerably reduced if simulation models are used to eliminate most of the unworkable alternatives. Since drying models are used in the decision making process of an automatic controller, advances in this area would normally affect the ability to control the drying process.

A lot of work however remains to be done in the development of good and reliable drying models. Many drying parameters are yet to be determined because of lack of reliable methods of measuring them or the lack of scientific knowledge related to the behavior of these parameters under dynamic drying conditions.

Symbols

C_a	Specific heat of dry air, $\text{J kg}^{-1}\text{C}^{-1}$
C_g	Specific heat of dry product, $\text{J kg}^{-1}\text{C}^{-1}$
C_v	Specific heat of water vapour, $\text{J kg}^{-1}\text{C}^{-1}$
C_w	Specific heat of water, $\text{J kg}^{-1}\text{C}^{-1}$
D	Moisture diffusivity coefficient, m^2s^{-1}
G	Specific mass flow rate of air, $\text{kg m}^{-1}\text{s}^{-1}$
G_p	Specific mass flow rate of product, $\text{kg m}^{-1}\text{s}^{-1}$
h_a	product volumetric heat transfer coefficient, $\text{J m}^{-3}\text{C}^{-1}\text{s}^{-1}$
h_{fg}	heat of water desorption from free water surface, J kg^{-1}
h_{fg*}	heat of water desorption from a drying product, J kg^{-1}
K	drying rate constant, s^{-1}
K_{ii}	Luikovs phonological constants
k	Thermal conductivity, $\text{J }^\circ\text{C}^{-1}\text{m}^{-1}$
i	drying layer
M	moisture content of product, decimal dry basis, $\text{kg [kg of dry mater]}^{-1}$
M_e	moisture content of product under equilibrium conditions, decimal dry basis, $\text{kg [kg of dry mater]}^{-1}$

M_o	moisture content of product initial, decimal dry basis, kg [kg of dry mater] ⁻¹
t	time, seconds, minutes or hours
δt	time increment, seconds, minutes or hours
δx	depth increment, m
P_a	air pressure, pascals
P_v	Vapour pressure, pascals
P_{sv}	saturated vapour pressure, pascals
R	universal gas constant, kJ kg ⁻¹ K ⁻¹
RH	relative humidity, ratio of vapour pressure to saturated vapour pressure
T	air temperature, °C
T_{abs}	absolute temperature, Kelvin
t	time, seconds, minutes or hours
θ	air temperature, °C
ε	void ratio
ρ_a	air density, kg m ⁻³
ρ_g	product density, kg m ⁻³
W	absolute humidity of air kg [kg of dry air] ⁻¹

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Chapter 6

CANNING TECHNOLOGY – RECENT ADVANCES THROUGH OPTIMIZATION AND MODELLING TECHNIQUES

Emmanuel Ohene Afoakwa^{1,2*}

¹Centre for Food Quality, SIPBS, University of Strathclyde, Royal College Building, 204
George Street, Glasgow G1 1XW, United Kingdom

²Department of Nutrition and Food Science, University of Ghana, P. O. Box LG 134,
Legon – Accra, Ghana

Abstract

Canned foods are a significant component of the diet of most people in both developed and developing countries, offering a wider choice of nutritious, good quality foods in a convenient form all-year-round. During canning, both desirable and undesirable changes occur in nutritional and sensory properties of foods, resulting from heat treatment employed for the destruction of microorganisms to achieve the desired commercial sterility. The extent of thermal processing, in terms of both temperature and duration of the treatment, is dependent upon the chemical and physical composition of the product, the canning medium and the conditions of storage, determining the product quality in terms of its sensory properties and nutrient content. This chapter reviews the major principles and operations used during food canning, identifies the nutritional and sensory changes occurring during the process and their effect on the quality of canned foods. In addition, it explains the use of response surface methodology (RSM) as modelling and optimization techniques used in the canning industry in recent times to manipulate canning processes to maintain the nutritional and sensory qualities of canned foods, using two recent studies where RSM was used to study the effect of pre-canning processes including blanching time, soaking time and sodium hexametaphosphate $[(NaPO_3)_6]$ salt concentration on moisture, minerals, leached solids, phytates, tannins and hardness (texture) of cowpeas (*Vigna unguiculata*) and bambara groundnut (*Voandzei subterranea*). Regression models were developed to predict the pre-canning parameters that yield the best quality products, with minimal effects on the nutritional and textural properties of the products. The optimal conditions found to achieve the optimum quality of the canned cowpeas were blanching time of 5 min, soaking time of 12 h and

* E-mail addresses: e_afoakwa@yahoo.com, e.afoakwa@strath.ac.uk, Tel: +44 (0) 7984288727

[(NaPO₃)₆] salt concentration of 0.5%, and for the bambara groundnut; blanching time of 8 min, soaking time of 12 h and [(NaPO₃)₆] salt concentration of 0.5%. The combination of blanching, soaking and [(NaPO₃)₆] salt were modeled using RSM to retain the nutritional (mineral) content of products while reducing the anti-nutritional factors and the hardness of the canned products with acceptable quality characteristics, indicating that as recent advances in canning technology, modelling techniques could be used to control canning operations while retaining desirable product quality characteristics.

Keywords: Canning; thermal processing; nutritional quality; sensory quality; modelling; optimization; response surface methodology.

Introduction

Canning is a fairly old technology used for the preservation of a wide variety of foods, producing safe and shelf-stable canned food, and has been the cornerstone of food processing industry over the past two centuries. The techniques used have been founded on scientific evidence following developments in food microbiology, heat transfer mechanisms, thermal processing and container closure technology. The canning industry now produces tens of millions of canned foods on a daily basis, with 40-70% of a harvest likely to be preserved by canning, depending on the country and type of food.

The primary purpose of canning is to protect public health and safety. The principal public health concern in canned foods is spoilage by *Clostridium botulinum*, a dangerous heat resistant microorganism which grows in anaerobic (oxygen-free) environments. If a canned product does not receive proper heat treatment, there is an increased risk that this organism could survive and produce a potent toxin within the container that when consumed, could prove fatal to consumers. It is an absolute requirement that a food manufacturer institute policies and procedures to prevent such an occurrence. The canning process is most often associated with applying heat to foods before or after being filled and double-seamed or heat-sealed in hermetically (air-tight) containers which can be made of metal, glass, polymeric or other composite materials. Inhibitors or “barriers” to microbial growth, such as pH, total acidity, other chemicals and/or available product water, can be used in combination with heat to either destroy or inhibit the growth and toxin production of all microorganisms capable of spoiling the food under non-refrigerated conditions of storage and market distribution. This includes all microorganisms capable of causing human illness (public health significant). Over-treating products with heat can lead to issues that make the product quality unacceptable for sale (e.g. mushiness, darkened color, burned flavor, vitamin degradation) (Lopez, 1987; Downing, 1996). Thus, cautious scientific approach is used to establish the thermal process requirement meeting both needs of product safety and quality. There is generally fine “balance” between designing and delivering a process for product safety while ensuring important sensory and nutritional quality characteristics.

The extent of thermal processing, in terms of both temperature and duration of the treatment, is dependent upon the chemical and physical composition of the product. Both physical and chemical changes occur during processing and, to a lesser extent, during storage, and it is these that determine the product quality in terms of its sensory properties and nutrient content. These changes, which can be either desirable or undesirable, are influenced by the time and temperature of the process, the composition and properties of the food, the canning

medium, and the conditions of storage. Several changes occur during canning influencing the nutritional and sensory properties of foods, primarily through damages to heat-labile nutrients and physical loss of nutrients due to leaching (Lopez, 1987; Downing, 1996; Pither, 2003; Ko *et al.*, 2007; Patindol *et al.*, 2007). In recent years, advances in canning technology has been geared towards the application of modelling and optimization techniques using response surface methodology to manipulate process designs during canning to control the detrimental effects on physical damage, nutrient loss associated with canned foods (Silva *et al.*, 1992; Omar & de Silva, 2000; Chen & Ramaswamy, 2002; Ibanoglu & Ainsworth, 2004; Ismail & Revathi, 2006; Simpson *et al.*, 2006; Simpson *et al.*, 2007).

Response surface methodology (RSM) is a statistical-mathematical method which uses quantitative data in an experimental design to determine and simultaneously solve multivariate equations, to optimize processes and products. It has been very popular for modelling and optimization studies in recent years and several authors have used it to optimize canning processes (Omar & de Silva, 2000; Ibanoglu & Ainsworth, 2004; Ismail & Revathi, 2006; Afoakwa *et al.*, 2006). RSM is used not only for optimization but also for determination of kinetic constants and investigation of optimal pre-processing and processing parameters that could enhance nutrient stability and minimal changes in physical quality of canned foods. Nowadays, it is clearly seen that RSM has been widely applicable for different purposes in physical and biochemical processes.

This chapter reviews the principles and operations of food canning processes, identifies the nutritional and sensory changes that occur during canning and their effect on the quality of canned foods. Using two studies, it evaluates application of response surface methodology as modeling tool for optimizing and/or controlling canning operation, to yield the best quality products while retaining their desirable nutritional and sensory qualities.

The Canning Process

History of Canning

The science of “canning” is one of the oldest and most widely used food preservation techniques and it is credited to Nicolas Appert, who published a book in 1810 on its processes using hot water bath termed “Appertization”. The book was later translated into English and gained wide acceptance and adoption in the 20th century in many countries. His method of preservation was primarily aimed at the elimination of microorganisms of public health concern using large quantities of sugar, salt, and vinegar as preserving agents. Later, he developed several food preservation methods into procedures that not only prevented large economic losses associated with microbial spoilage, but also destroyed food-borne microorganisms that were capable of causing illness, or even death, in humans (Lopez, 1987; Downing, 1996; Berry & Pflug, 2003).

Principles and Operation

Canning is the general term applied to the process of packaging food in a container and subjecting it to thermal processing for the purpose of extending its shelf life. An optimal

thermal process destroys pathogenic (disease-causing) bacteria, kill or control spoilage organisms present, and have minimal impact on the nutritional and physical qualities of food. The cans used are usually thought of to be made of steel or possibly aluminum, the principles apply equally well to a variety of food containers such as glass jars, plastic and foil-laminated pouches, semi-rigid plastic trays or bowls, as well as metal cans of any one of several shapes, including cylindrical, oval, oblong, or rectangular. The concept of aseptic packaging (sterilization of food and its container prior to filling and sealing) also follows the same principles (Berry & Pflug, 2003).

Canning by thermal processing coupled with hermetic packaging is used to preserve a wide variety of products, the basic function of which is to inactivate pathogenic and food spoilage micro-organisms in sealed containers of foods using heat treatments at temperatures well above ambient boiling point of water in pressurized steam retorts (autoclaves). Microbial control processes at temperatures in the 65–95 °C range are often called pasteurization, those from 100 to 150 °C, sterilization. Pasteurization processes are designed to kill pathogenic microorganisms and extend product life under refrigerated storage; sterilization processes make possible indefinite product life at ambient temperatures. Whereas the principles of thermal process design are the same for all conditions, the concepts for process establishment that will follow are those for the sterilization of foods known as low-acid canned foods (LACFs) packaged in hermetically sealed containers (Downing, 1996; Berry & Pflug, 2003; Simpson *et al.*, 2006).

Microorganisms of Concern

Clostridium botulinum, which is the most heat resistant, mesophilic, anaerobic spore-forming pathogen, is the target microorganisms of canning, as it is capable of growing and producing toxins in shelf-stable canned foods, of which one millionth of a gram can kill a human. *C. botulinum* is ubiquitous; occurring in both cultivated and forest soils, sediments of streams, lakes, and coastal waters, the intestinal tracts of fish and mammals, and gills and viscera of crabs and other shellfish. For many years, laboratories in canning industries have devoted much attention to *C. botulinum*, and retorting, a sterilization process aimed at destroying pathogenic and non-pathogenic heat resistant spores generally operate at temperatures $>105^{\circ}\text{C}$ – $<130^{\circ}\text{C}$ for a sufficient time to destroy both non-heat resistant microbial vegetative cells in addition to heat resistant microbial spores in food products.

In addition to *C. botulinum*, retort processes are designed to also destroy other non-pathogenic mesophilic, anaerobic spore-formers such as *C. sporogenes*, a non-toxic sister organism to *C. botulinum*, but has an *even higher* heat resistance than *C. botulinum*. Many commercial processes for low-acid canned foods in hermetically sealed containers processed in retorting applications are safely established upon the heat resistance of *C. sporogenes*. There are numerous other spoilage organisms that pose spoilage issues due to microbial recontamination through the double seam or heat seal, and those that can grow at higher than normal storage temperatures. Also, in some cases, for example, salt, nitrate and nitrite, sugar, reliance on naturally occurring product pH, organic acids and bacteriosins can reduce the retort process for low-acid and some acidified foods which have within a general range of $\text{pH}>4.5$ – <5.2 .

Thermal Resistance of Microorganisms

Thermal resistance of microorganisms including vegetative cells and spores varies. The relation of the core components of a spore to heat resistance is mainly dependent on pH. As pH has profound effects, thermal processing has been divided into three categories based on the level of pH or acidity of foods;

- i. high acid foods (pH less than 4.0)
- ii. acid foods (pH between 4.0 and 4.6) and
- iii. low-acid foods (pH greater than 4.6).

The basis for this decision was that, at a pH of less than 4.6, *C. botulinum* will not grow to produce toxins, but at pH above 4.6, in a favorable medium *C. botulinum* will multiply and produce toxins. Examples of foods with a pH greater than 4.6 are vegetables, fresh meats, and seafood. Tomatoes normally have pH less than 4.6 and require less severe heat treatment (pasteurization) to achieve preservation. Water activity (a_w) is a measure of the amount of available water in the food. The a_w of fresh fruits, vegetables, and meats is normally greater than 0.85. Dried fruits, honey, and salami have insufficient water content to support the growth of most hazardous microorganisms and thus do not require sterilization processes to produce shelf-stable products (Azizi, 1999).

Determination of Thermal Resistance of Microorganisms and Process Lethality

There are three microbiological parameters which are involved in all process establishment work, namely D_T , z , and F - values. These variables define the thermal resistance of bacteria and indicate how much of an effect a particular thermal process is likely to have.

D_T-value:

The D_T value, which is defined graphically in Fig. 1a, is the time in minutes at constant temperature (T) to inactivate 90% (one log reduction) of the target organisms present in a food. The D_T value is also known as the 'death rate constant' or 'decimal reduction time'. Thermal resistance, or thermal destruction tests (TDTs), that measure D_T are conducted using small food samples inoculated with known levels of microorganisms. The samples, contained in specially designed, low-profile TDT cans or glass tubes, are heated in chambers capable of rapidly heating the sample to a precise temperature, holding for a precise time period, and rapidly cooling to sub-lethal temperatures. Common heating devices are the TDT retort and the thermo-resistometer (Berry & Pflug, 2003).

A plot of the thermal resistance (or survival) data must approximate a straight line on semi-logarithmic graph paper (Fig. 1a) for the D_T value to be meaningful. Each TDT curve is unique for the microorganism, food medium, and exposure temperature. The D_T value describes the time effect of heat on a population of microorganisms exposed at constant temperature for a precise time period, without influencing heating (come-up) or cooling period effect. Berry and Pflug (2003) explained that the $D_{121.1^\circ\text{C}}$ value for *C. botulinum* is normally taken as 0.2 min. This is based on thermal resistance studies conducted in the early

1920s on spores harvested from the most heat-resistant strains known. These studies demonstrated that, by extrapolation from the semilogarithmic survival curve, it was necessary to heat a spore suspension in phosphate buffer for 2.78 min at 121.1 °C to reduce the survival population from about 10^{11} spores per unit to less than one spore per unit (12-log reduction). Later, correcting the data for come-up time resulted in a reduction of the heating time to 2.45 min to achieve the same lethal effect, hence, a $D_{121.1^{\circ}\text{C}}$ value of 0.2 min. To be efficient in the thermal process design, there is need to take advantage of the microbial kill at each step along the thermal process path, and this is defined by the z-value.

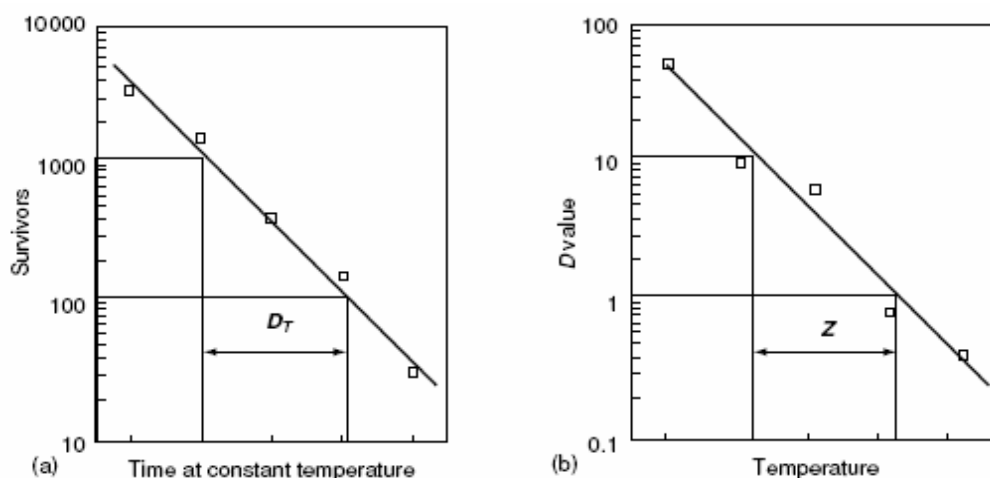


Figure 1. Graphical representation of D and z-values; a. D-value; time required at temperature to reduce survivors by 90%; b. z-value; temperature change required for a 10-fold change in destructive rate (from Berry & Pflug, 2003).

z-value:

The z-value denotes the number of degrees of temperature required to effect a 10-fold change in the time to achieve the same lethal effect. A higher z-value means that a greater change in process temperature is required for the same change in the destruction rate of an organism. The z-value makes it possible to quantify the microbial kill at the product temperature that exists at all times during a thermal process. The thermal resistance curve shown in Fig. 1b illustrates the z-value. A series of TDT tests are conducted to determine the effect of different temperatures (D_T values) on the thermal resistance of an organism. By plotting the measured D_T values on a logarithmic scale against temperature on a linear scale (Fig. 1b), a thermal resistance curve is constructed. The thermal resistance curve relates time for a one log kill with the kill temperature. From this plot, the z-value can be obtained; it is the inverse slope of the curve and represents the number of degrees of temperature required for the curve to traverse one log cycle. The z-value allows is used as an index for calculating the lethal effect of various temperatures on the destruction of microorganisms. A range of z-values from 7°C to 12°C have been measured over the years for *C. botulinum*. These differences are attributed to the spore type (strain), heating system, test substrate, and method of calculation (Berry & Pflug, 2003).

For a given thermal process, the microorganism's destruction result can be expressed as the equivalent F-value at a reference temperature (F_0 value often used for the low-acid foods). The calculation of the F_0 value has been described in Equation 1. However, for a given product, it is critical to design a F_0 value so commercial lethality will be delivered to the product. The establishment of the sterilizing value (F_0) for a low-acid food product is one of the most critical responsibilities assumed by persons acting on behalf of a food company in the role of a competent thermal processing authority.

According to the definition of the F-value, the heating time, t , is actually the lethality or kill time, or F-value. If the heating temperature is 250°F (121.11°C), and heat resistant mesophilic spores are considered, then the equation can be written as:

where in Equation 1, D_{250} ($D_{121.11}$) is the decimal reduction time at 250°F (121.11°C). Alternatively, the F_0 value can also be expressed as in Equation 2 below:

Where:

- t = heating time at a constant temperature, T;
D = decimal reduction time at temperature, T;
N₀ = initial concentration of the microbial cells or spores;
N = number of survivors after t time heating.

Generally, Equation 1 is referred to as the straight-line semi-logarithmic model, which serves as the basic equation for the F_0 value establishment. The initial load of mesophilic spores before sterilization, N_0 , is described as “bioburden”. The final spore survivor numbers after a delivered thermal process is generally referred to as the probability of a nonsterile unit (PNSU). The unit may be a whole container, or weight or volume of the food. Therefore, the required F_0 value for a given product will depend on the product itself, the product bioburden (N_0), and the resistance of the target microorganism (D-value). Simpson *et al.* (2007) noted

that control of thermal process operations in food canning factories has traditionally consisted of maintaining specified operating conditions that have been predetermined from product and process heat penetration tests, such as the process calculations for the time and temperature of a batch cook, which in general is aimed at attaining commercial sterility.

Commercial Sterility

Commercial sterility is the term used to describe the condition of heat, chemically treated or irradiated product and packaging to render the packaged food shelf stable, free of viable microorganisms of public health significance and non-health significance capable of reproduction under normal non-refrigerated conditions of storage and distribution. Foods are required to be processed for a sufficient time at a sufficient temperature under controlled product and packaging conditions to achieve this outcome. For irradiated foods, a required radiation “dose” is delivered to the food and packaging which destroys microorganisms present without heating the food or packaging material in order to achieve shelf-stability. Proper container sealing also prevents the re-introduction of microorganisms found external to the container contents, within the environment, after the microbial reduction treatment is applied. Commercial sterility, as discussed above and “sterile” are often interchanged. The term “sterile” suggest the absence of all viable microorganisms, absence of pathogenic (public-health concern) organisms, or free of potential “spoilage organisms (commercial sterility) (Lopez, 1987; Downing 1996; Berry & Pflug, 2003).

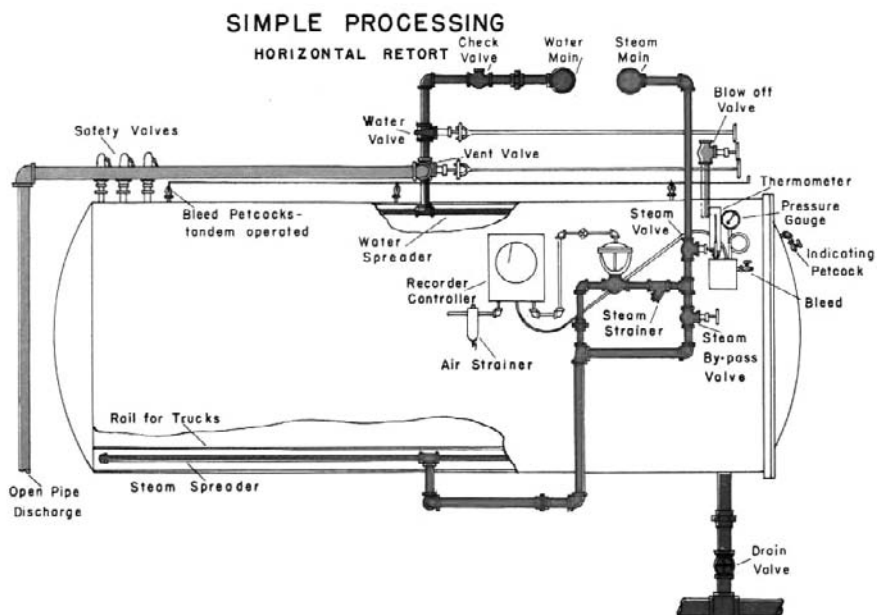
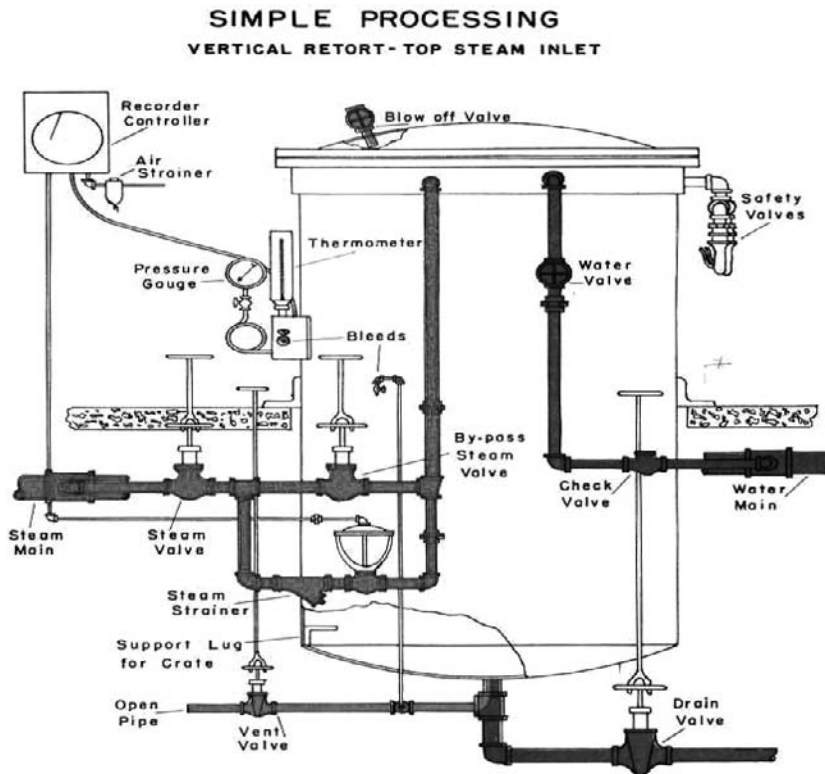
Canning Techniques in Food Processing Applications

A. Pasteurization

Canned products and packaging which are heat-treated may be either “pasteurized” or “sterilized”. If food is *pasteurized*, it is normally processed for sufficient time at a temperature $<100^{\circ}\text{C}$ in a hot water bath or flowing steam tunnel. In some cases a product may be pasteurized in a retort at temperatures $>100^{\circ}\text{C}$ $<105^{\circ}\text{C}$. The amount of acidulant associated with the food (pH and/or total acidity), if at sufficient sustainable levels, serves to inhibit the outgrowth of heat resistant organisms, including heat resistant spores (protected cells), that could cause public health or economic spoilage. The presence of a proper pH, in combination with a sufficient heat treatment over sufficient time, will destroy vegetative cells and non-heat resistant spores. Typically, high acid or acidified foods with a pH of < 4.5 are pasteurized.

B. Sterilization

Retorts generally operate at temperatures $>105^{\circ}\text{C}$ $<130^{\circ}\text{C}$ for a sufficient time to destroy both non-heat resistant microbial vegetative cells and spores in addition to heat resistant microbial spores in the product. If the food is “sterilized”, the principal piece of equipment used is a “retort” (Figs. 2 and 3), an unfired pressure vessel which employs steam, steam heated hot water or high velocity steam/air mixtures under pressure, principally to low-acid (>4.5) products.



C. Retorting

The retort (Figs. 2 and 3) is designed to process containers in either a batch or continuous mode. In batch retorts, there is a cycle which is applied to every individual load of containers that requires a heating step in the vessel to sterilization temperature, holding the container load at a temperature for a sufficient period of time, and then introducing a cooling medium to the load to properly cool the container load. Every container in the retort load experiences a similar process exposure at any given time interval. In continuous retorts, the retort is initially brought up to an operational temperature condition before containers are introduced. The process temperature is generally steady state. Unlike the batch retort, each container has a distinctly different process history at any given time step. Some batch and continuous retort designs offer container rotation during the thermal process. For certain products which are processed with a controlled container headspace, this container movement can increase the heat transfer rate and thus reduces the thermal process requirement.

D. Aseptic

In other canning applications, heat treatment is separately applied to both the product and the package. The product and package are brought together in a sterile environment. This canning application is termed “aseptic” processing. The packaging and environment where both product and packaging are assembled can be heat treated or chemically treated or both. Packaging can also be pre-sterilized by ionizing radiation before it is filled and sealed in a sterile environment.

During canning, excessive heat treatment should be avoided because it is detrimental to food quality and underutilizes plant capacity. Batch processing with a battery of individual retorts is a common mode of operation in many food-canning plants (canneries). Although high speed processing with continuous rotary or hydrostatic retort systems can be found in very large canning factories (where they are cost-justified by high volume throughput), such systems are not economically feasible in the majority of small to medium-sized canneries. Many studies have shown that maximum nutrient retention at constant retort temperature does not differ considerably from the one obtained from time variable retort temperature processes (VTRT) when optimizing average quality (Almonacid-Merino *et al.*, 1993; Saguy & Karel, 1979; Silva *et al.*, 1992).

Quality Changes During Canning

Changes in Nutritional and Sensory Properties of Foods

Both physical and chemical changes occur during canning of foods, causing both desirable and undesirable changes in their nutritive value and sensory characteristics. The thermal process employed can cause damage to heat-labile nutrients and physical loss of nutrients due to leaching. Also, many reactions occur during canning that affect the availability of nutrients within foods, affecting their usefulness to the body.

Table 1. Changes in nutritional and sensory qualities of foods during canning

Attribute	Effects	Foods affected
<u>A. Nutritional properties:</u>		
Water	Loss of total solids into canning liquor Dilution Dehydration	Legumes, tomatoes, fish Vegetables, fruits
Proteins	Enzymic inactivation Loss of certain essential amino acids Loss of digestibility Improved digestibility	Milk Milk, eggs, meat Meat Legumes, milk
Carbohydrates	Starch gelatinization Increased digestibility	Cereals, legumes, root crops Legumes, root crops
Dietary fibre	Loss of physiological value	Fruits, vegetables
Lipids	Conversion of cis fatty acids to trans fatty acids Loss of essential fatty acid activity	Meat, fish Meat, fish
Fat-soluble vitamins	Increased bioavailability of biotin and nicotinic acid due to enzyme inactivation	Milk Fruits, vegetables
Water-soluble vitamins	Large losses of vitamins C and B1 due to leaching and heat degradation	Fruits, vegetables
Minerals	Possible increase in sodium and calcium levels by uptake from canning liquor Losses due to oxidation of lipids Mainly heat-stable Losses due to leaching	Meat, fish, legumes Fish Legumes, fish, meat Legumes, fish, meat, vegetables

Table 1. Continued

Attribute	Effects	Foods affected
<u>B. Sensory properties:</u> Flavour - Volatile loss (scalping oxidation) - Volatile formation - Maillard - Oxidation - Pyracaines Texture - Cell membrane damage - Cell separation - Protein denaturation - Starch gelatinization Colour - Natural pigment breakdown - Maillard reactions - Others, e.g., metals and polyphenolic compounds	Loss of flavour Roasted flavour, bitterness Rancidity Roasted flavour Loss of cellular water and solutes, loss of crispness Tissue softening, loss of firmness and tissue turgor Gelling, firming Gelling Bleaching; loss of colour Browning Discoloration	Meat, fish Legumes, cereals, meat Meat, fish Meat, rice pudding, Legumes, fruits, vegetables Legumes, vegetables, fruits Meat, fish Cereals, root crops Vegetables, fruits Meat, nuts, beans, fish, milk Asparagus, pears, peaches

Sources: Pither (2003); Harris & Kamas (1988); Lund (1982); Richardson & Finley (1985).

Inadvertently, the sensory properties of foods, including flavour, colour, and texture can all be affected by the thermal processing. Changes in these properties may be in the form of direct effects of heat on food constituents (e.g., starch gelatinization, protein denaturation, and cell separation) or through heat-induced reactions such as the Maillard reaction. Significant changes in all three sensory properties can also be brought about by oxidation reactions that can occur, not only during processing, but also on subsequent storage of the canned product. Oxidation reactions in fruits and vegetables occur mainly during preparation prior to processing, due to the effects of oxidative enzymes. Heat treatments, such as blanching prior to canning and the sterilization process itself, cause inactivation of these enzymes. Along with the low oxygen tensions in canned products, this limits oxidation in all but the most oxygen-sensitive constituents (Pither, 2003). Table 1 provides a summary of some changes in nutritional status and sensory properties during canning.

Modelling and Optimization Techniques in Canning Technology

The Need for Modelling or Process Optimization

The quality of canned food is dependent on many factors such as pre-processing conditions, retort temperature and time, can size and shape, thermal properties and kinetic parameters. To obtain the best quality product at consistent production rates, each combination of food product and container geometry requires different processing procedures making selection of processing parameters a multi-factor optimization problem, specific to every product. Saguy (1983) noted that solving optimization problems consist of two steps:

- (i) the development of models for the objective function using mathematical approaches which could include regression models, theoretical analysis models or differential equations,
- (ii) the identification of optimal conditions which are searched using a search method such as direct search, grid search or gold section method for a single variable, or alternating variable search, pattern search or multiple variables analysis.

However, with the rapid development of computer technology and software, modeling and optimization techniques using response surface methodology has gained prominence in the food canning industry in recent years and have been found to offer advantages over conventional methods to deal with system modeling and optimization problems, especially for canning processes involving multiple pre-processing conditions employed to influence desirable changes in physical and biochemical constituents of canned foods.

Modelling and Optimization Processes using Response Surface Methodology (RSM)

During food processing, it is important to improve the performance of the systems employed to increase efficiency of the processes involved for enhanced product quality without affecting the production time and cost, and these can be achieved by a technique known as

process optimization. This can be achieved by manipulating some of the processing parameters to determine the optimal operating conditions while keeping other factors at constant level. In recent times, application of modelling or optimization processes have found use in canning technology to determine optimal processing conditions to achieve the best quality product while maintaining high nutrient retention and other product quality characteristics. The techniques employ interactive effects among the variables to depict an eventual complete effect on the processing parameters. This optimization studies are carried out using response surface methodology (RSM).

RSM is a collection of statistical and mathematical techniques used for developing, improving, and optimizing processes in which a response of interest is influenced by several variables and the objective is to optimize the response. RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the physical or biochemical processes (Anjum *et al.*, 1997; Myers & Montgomery, 1995). It consists of a group of mathematical and statistical techniques that can be used to define the relationships between the response and the independent variables. RSM defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology also generates a mathematical model. The graphical perspective of the mathematical model has led to the term Response Surface Methodology (Baş & Boyacı, 2007a).

Optimization studies using RSM could be separated into three stages. The first stage is the preliminary work in which the determination of the independent parameters and their levels are carried out. The second stage is the selection of the experimental design and the prediction and verification of the model equation. The last one is obtaining the response surface plot and contour plot of the response as a function of the independent parameters and determination of optimum points (Baş & Boyacı, 2007a).

Several authors have reviewed the use of RSM for the optimization of physical, chemical and biochemical processes in food processing due to its wide application in the modern food industry (Griffin & Stauffer, 1990; Joglekar & May, 1991; Anjum *et al.*, 1997; Myers & Montgomery, 1995; Baş & Boyacı, 2007a; Baş & Boyacı, 2007b).

Advantages of RSM

Baş and Boyacı (2007a) explained that RSM has several advantages compared to the classical experimental or optimization methods in which one variable at a time technique is used. Firstly, RSM offers a large amount of information from a small number of experiments. Indeed, classical methods are time consuming and a large number of experiments are needed to explain the behavior of a system. Secondly, in RSM it is possible to observe the interaction effect of the independent parameters on the response. Especially in biochemical processes, the interaction effect of the parameters would be more critical such as synergism, antagonism, and addition. The model equation easily clarifies these effects for binary combination of the independent parameters. In addition, the empirical model that related the response to the independent variables is used to obtain information about the process. These factors make

RSM a useful tool for the modelling and optimization of physical and biochemical processes of foods.

Application of Response Surface Methodology for Process Optimization During Food Canning Operations

Study One: Canning of Cowpea (*VIGNA UNGUICULATA*)

Response surface methodology for studying the influence of soaking, blanching and sodium hexametaphosphate salt concentration on some biochemical and physical characteristics during canning of cowpeas (*Vigna unguiculata*)

Background

Cowpea (*Vigna unguiculata* L. Walp) also known as black eye peas, is one of the most commonly utilized legumes in Africa. It is an important crop in some areas of the tropics where it provides more than half the plant protein in human diets. It is highly nutritious with a dry seed protein content of about 25% and protein digestibility higher than that of other legumes (Olonghobo & Fetuga, 1983; Afoakwa *et al.*, 2002). Cowpea is cultivated extensively, mostly in the savannah areas of West Africa, and in Nigeria and Ghana it is referred to as beans. It has been found to contribute up to 80% of the total dietary protein intake in some parts of West Africa. Many varieties of cowpea seeds exist and are known by their different sizes, shapes and especially seed colour which can be either white, red, brown, black, cream and mottled (Sefa-Dedeh *et al.*, 2001; Afoakwa *et al.*, 2007).

Cowpeas constitute about 52% of the total world output of grain legumes. Major cowpea producing Countries in the world include Niger, Nigeria, U.S.A., Burkina Faso, Brazil, Ghana and Uganda. Cowpeas are consumed in various forms such as green pods, tender green leaves, green seeds and dry seeds. Usually the processing of cowpeas for consumption involves mainly traditional methods. These methods include soaking, dehulling, steaming and cooking by boiling in excess water. An important feature of cowpeas with respect to other legumes is their high protein content. Some varieties of cowpeas available in Ghana have a protein content ranging from 24% to 27% (Afoakwa *et al.*, 2002).

To make cowpeas edible and to increase their shelf life, they are usually processed and preserved by cooking or sterilisation of the dry beans to develop acceptable flavour, texture, and inactivate anti-nutritional factors to make the bean protein nutritionally available to human life. This process usually involves the soaking of the cowpeas in water, draining and cooking or sterilizing in fresh boiling water or brine. Factors such as storage conditions, soaking treatment and cooking method influence the cook ability or sterilizability and acceptability of the cowpeas (Phillips & Mcwatters, 1991; Afoakwa *et al.*, 2004). Some research efforts have led to the gradual development and adoption of various preservation methods to make cowpea available all year round. In most developed countries, cowpeas are packaged dry, either raw or precooked, canned in water, tomato sauce or molasses; and canned in combination with other vegetables and meat or as constituents of soups, salads and

dips. Even though traditional drying method of cowpea is economically cheaper, canning is proven to give cowpea a longer shelf life (Bressani, 1993). The canning industry is constantly improving processing methods, enhancing quality and product safety. Processing methods designed, heighten retention of nutrients and effective use of energy. Pre-canned cowpea is usually soaked in cold soft water for 10 to 12 h, although an occasional lot may require somewhat less soaking depending on the moisture content of the peas and the hardness of the water (Lopez, 1987).

Research on other legumes has shown that the digestibility of macronutrients and bioavailability of minerals are affected by factors such as the cellular anatomy of legume products and their levels of naturally occurring complex-forming 'anti-nutritional' substances such as phytate and (poly)phenolic compounds. Phytic acid forms complexes with minerals such as Zn and Fe, which lowers their bioavailability (Eyzaguirre *et al.*, 2006). The soaking operation varies with the condition of the raw cowpeas and it has reported to cause a significant decrease in anti-nutrients, as the anti-nutrients are leached into the soak water (Lopez, 1987). Soaking for 18 hours removed 65% of hemagglutinin activity in peas and soaking for 24 hours at room temperature removed 66% of the trypsin (protease) inhibitor activity in mung beans, 93% in lentil, 59% in chickpea and 100% in broad bean. Other components lost are tannins, phytates and oligosaccharides. The loss of nutrients can be minimised through the soaking of whole seeds. The soaking solution employed has significant effect on the texture of the beans. Water with 4 to 9 grains hardness is considered ideal for soaking and blanching cowpeas and an addition of 0.2% Sodium hexametaphosphate has been found to be satisfactory in water having 26 to 29 grains total hardness per gallon (Lopez, 1987). Sodium hexametaphosphate has been used in the canning industry for decades as an acceptable food additive, and it is used generally for the purpose of stabilising or improving texture of dried peas or seeds. As new cowpea varieties are developed for human consumption by the use of canning techniques, it is important to study the influence of soaking, blanching and sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ salt concentration on the nutritional, anti-nutritional and physical characteristics of the newly developed cowpea (*Vigna unguiculata*) seeds.

This study aimed at evaluating the influence of soaking, blanching and sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ salt concentration on some nutritional, anti-nutritional and physical characteristics of cowpea (*Vigna unguiculata*) seeds during canning using response surface methodology.

Materials and methods

Materials

Cowpea seeds (IT87D195Y) was obtained from the Crop Research Institute of the Council for Scientific and Industrial Research (CSIR) of Ghana and used for the study.

Experimental design for response surface methodology

A Central Composite Rotatable Design (CCRD) of the experiment was set up using the Statgraphics software with experimental study variable number $K = 3$, for independent variables including blanching time (X_1), soaking time (X_2) and sodium hexametaphosphate

concentrate (X_3). The process variables to be used in the CCRD for $K = 3$ were processed using the Statgraphics Plus software. This will indicate the dependent variable limits and their values. The dependent variables studied included the following: moisture content of the canned cowpeas, ash content, leached solids, phytates, tannin content of canned product and hardness (texture) of canned cowpeas.

Table 2. Process variables and their levels used in the Central Composite Rotatable Design for $K=3$

Independent variables	Code	Variable Levels				
		-1.682	-1	0	+1	+1.682
Blanching time (mins)	X_1	0	2.03	5.00	8.00	10.00
Soaking time (h)	X_2	0	4.87	12.00	19.16	24.00
$[(NaPO_3)_6]$ (%)	X_3	0	0.20	0.50	0.80	1.00

Twenty sample combinations were generated from the software in experimental design using the design matrix and variable combinations in experimental runs as shown on Tables 2 and 3 below. The cowpeas were canned using tin cans with dimensions of 44.0 mm x 83.7 mm. The pre-processing conditions as indicated in the various combinations generated in the experimental design were conducted on the cowpeas and canned in a still vertical retort at 121°C (250°F) for 30 min. The data collated from the experiments conducted on the various combinations were then tabulated accordingly and analysed using stepwise regression analysis.

The Optimization Process

A stepwise multiple regression analyses was conducted on the data from the Central Composite Rotatable Design to relate blanching time, soaking time and sodium hexametaphosphate (salt) concentration, $[(NaPO_3)_6]$ to moisture content, ash content, leached solids, phytates, tannin content and hardness of the canned cowpeas. The response surface models were generated and presented as 3- dimensional plots in the function of 2 factors (blanching time and soaking time) whilst the salt concentration $[(NaPO_3)_6]$ is kept constant. Adequacy of the model equation for predicting optimum response values was tested in the experiment using the blanching time of 0-12 minutes, soaking time of 0-24 hours and salt concentration $[(NaPO_3)_6]$ of 0-1%. Three optimal processing conditions of the canning procedures of the cowpeas were determined from the mathematical models. In order to get these optimal values, the first partial derivatives of the regression equations were done according to X_1 , X_2 and X_3 and sorted.

Table 3. Design matrix and variable combinations in experimental runs

No. Serial No.	Level codes			Levels		
	BT (X ₁)	ST (X ₂)	SHPC (X ₃)	Blanching time (mins)	Soaking time (h)	Sodium hexameta phosphate conc. (%)
1	-1	-1	-1	2.03	4.87	0.20
2	-1	1	1	2.03	19.16	0.80
3	1	-1	1	8.00	4.87	0.80
4	1	1	-1	8.00	19.16	0.20
5	0	0	0	5.00	12.00	0.50
6	0	0	0	5.00	12.00	0.50
7	-1	-1	1	2.30	4.87	0.80
8	-1	1	-1	2.03	19.16	0.20
9	1	-1	-1	8.00	4.87	0.20
10	1	1	1	8.00	19.16	0.80
11	0	0	0	5.00	12.00	0.50
12	0	0	0	5.00	12.00	0.50
13	1.682	0	0	10.00	12.00	0.50
14	-1.682	0	0	0.00	12.00	0.50
15	0	1.682	0	5.00	24.00	0.50
16	0	-1.682	0	5.00	0	0.50
17	0	0	1.682	5.00	12.00	1.00
18	0	0	-1.682	5.00	12.00	0
19	0	0	0	5.00	12.00	0.50
20	0	0	0	5.00	12.00	0.50

BT - Blanching time

ST - Soaking time

SHPC - Sodium hexametaphosphate concentration

Sample Treatments

Equal amount of cowpea was treated with sodium hexametaphosphate concentrations of 0, 0.2, 0.5, 0.8 and 1%. The cowpeas were then soaked in the sodium hexametaphosphate solution respectively for 0, 5, 12, 19 and 20 h. The cowpeas prior to canning were blanched for 0, 2, 5, 8 and 10 min. The samples were then processed in a vertical retort for 20 min at 121°C.

Analytical Methods

Moisture Content Determination

The moisture content of the samples were determined using the AOAC (1990) method 950.40 of oven drying at 105°C for 6 h. The experiment was conducted in triplicate and the mean value determined.

Ash Content Determination

The ash content of the samples was determined using the procedure as outlined in the Association of Official Analytical Chemists' Approved method 14.41 (AOAC, 1990). The crucibles were heat dried at 600°C in a muffle furnace for 30min and cooled in desiccators. The crucibles were weighed and the initial weight noted. About 2 g of sample were weighed and ashed at 600°C in the muffle furnace overnight. It was then cooled and weighed and the percentage ash determined.

pH Measurement

pH was measured exclusively with glass electrode pH meter. The determination was done on a small amount of syrup poured from the can into a beaker and the pH of the drained liquid was determined using the TOA pH meter.

Drained Weight

After determining the fill of the container, the contents of the container was distributed over the meshes of a circular sieve made with a specified number (No. 8), that is, 8 holes/inch woven wire cloth which complies with the specifications for such cloth set forth in "Standard specifications for sieves". The diameter of the sieve used is 8 inches, without shifting the peas, the sieves were inclined to facilitate drainage. About two minutes after the drainage had began the cowpeas were removed from the sieve and weighed, and the drained weight of the cowpeas noted (Pearson, 1976).

Seed Splitting

The content of each container was distributed over the meshes of a circular sieve made with a specific number (8 holes per inch) woven wire cloth for liquid to drain. The weight of splitted cowpea was taken and expressed as a proportion of the total weight of the canned cowpeas.

Leached Solids

The leached solids in the samples were determined according to the procedure as outlined in Lopez (1997). A 10 ml aliquot of the drained water from samples after canning was dried at 105°C in an air oven for 24 h. The weight of the residue was determined after drying. This was done in triplicate and the mean value reported as g/g dry sample.

Phytic Acid and Tannin Determinations

The phytic acid and tannin levels in the samples were determined according to the procedure as outlined in Bainbridge *et al.* (1996).

Seed Hardness (Texture)

The hardness of seeds after canning was determined using a TA-XT2 Texture Analyser (Stable Micro Systems, Surrey, England). The test cell used was the Warner-Bratzler Blade.

The peak force required to cut through 5 seeds was determined. The seeds were placed longitudinally across the groove in the sample holder and cut perpendicularly across the axis of the seeds. The test conditions used were: test speed of 1.5 mm per second and distance of 11 mm. The test was replicated five times and the average peak force recorded.

Statistical Analysis

All the statistical analysis and graphical presentations were done using Statgraphics 5.1 (Graphics Software Systems, STCC, Inc, Rockville, USA). The significant probability was set at $p \leq 0.05$.

Results and Discussion

Effect of Pre-process Variables on Moisture Content of Canned Cowpeas

The model obtained for moisture content when the IT87D195Y cowpea was used for the canning was: $Z = 35.71639 - 0.54502X_1 - 0.59761X_2 - 14.30610X_3 + 0.01336X_1X_2 + 0.16250X_2X_3 + 0.04198X_1^2 + 0.01908X_2^2 + 11.04050X_3^2$ with an R^2 of 90.0%. There was a strong and significant influence of the quadratic factors of soaking time, salt concentration and blanching time as well as linear factors of blanching time and salt concentration on the moisture content. Statistical analysis conducted on the data showed that salt concentration and blanching time both had significant ($p \leq 0.05$) quadratic and linear effects on the model, with soaking time having only quadratic effect. The model could explain 90.0% of the variations in moisture content, meaning only 10.0% of the variation was due to other factors not included in the model. The response plots (Figs. 4a-4c) show that blanching time, soaking time and the salt concentration, all had significant effects on the moisture content of the canned cowpea with significant interaction between all the factors.

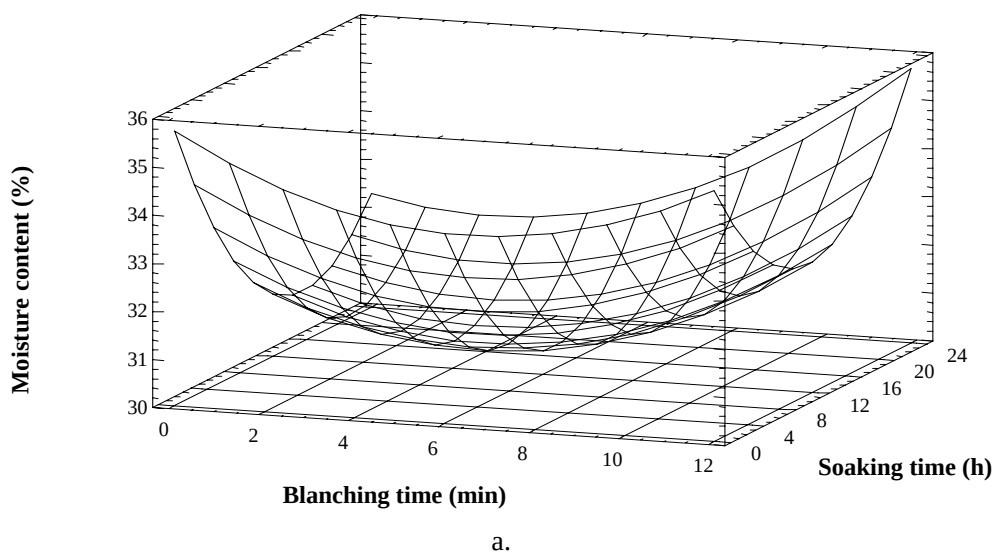
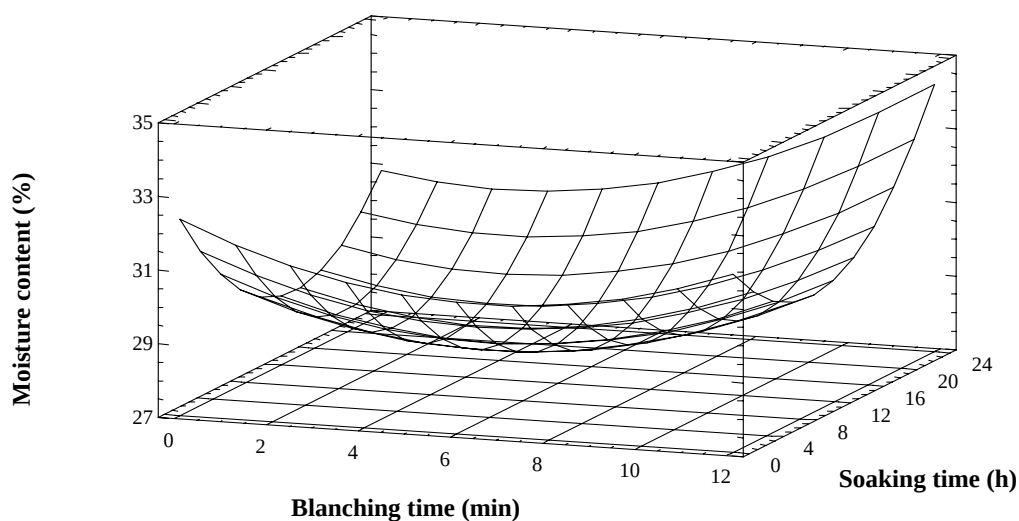
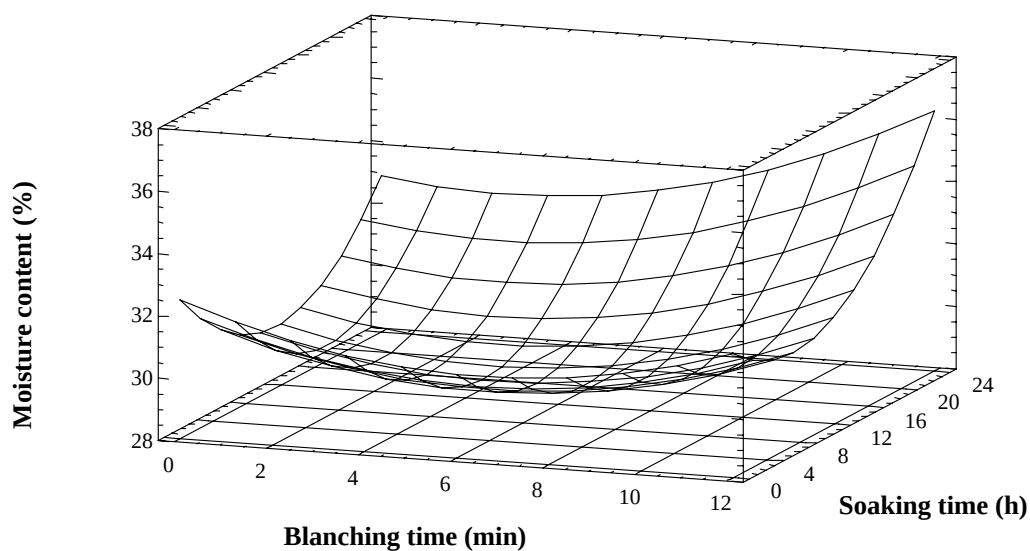


Figure 4. Continued on next page.



b.



c.

Figure 4. Response surface plot for moisture content of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

The response surface plots generated showed curvilinear plots with both blanching time and soaking time (Figs. 4a-4c). This implies that the moisture content of the cowpea seeds reduced slightly during the first few hours of soaking and then increased again till the end of the soaking time. Similar trends were observed for the blanching time with all the different salt concentrations used. Decreased moisture in canned food products have been reported to lowers the enzymatic deterioration as well as microbial and chemical activities in the product hence increases the shelf life of the product (Lopez, 1987).

Effect of Pre-process Variables on pH of Canned Cowpeas

The model obtained for pH of the canned cowpea was: $Z = 6.660304 - 0.08448X_2 - 2.30832X_3 + 0.00636X_1X_2 + 0.08965X_2X_3 - 0.00793X_1X_2X_3 + 1.73947X_3^2$, with an R^2 of 79.5%. There was a significant ($p \leq 0.05$) influence of the linear factors of soaking time and blanching time and the quadratic factor of the salt concentration. It was observed from the statistical analysis that both soaking time and blanching time had significant ($p \leq 0.05$) linear effect on the model, whilst the salt concentration had quadratic effect. The model could explain about 80% of the variations in pH. As shown in the response plots (Figs. 5a-5c), all the factors (blanching time, soaking time and salt concentration) had significant effects on the pH of the canned cowpeas. Increasing the salt concentration from 0.5% to 1.0% influenced the pattern of the pH with soaking times and blanching time, implying there were interactions between all the factors.

At 0% and 0.5% salt concentrations, the influence of blanching was not pronounced on the pH of the samples, hence very low pH levels were observed at the initial periods of blanching (Figs. 5a and 5b) which leveled up with increasing blanching times. On the contrary, the plots obtained for the cowpea soaked with 1.0% salt concentration showed that soaking influenced the pH of the canned cowpeas. The plot indicated that increasing blanching time and soaking time led to slight decreases in the pH of the samples (Fig. 5c).

pH is low when the cowpeas were blanching time of 5 min, soaking time of 12 h and salt concentration of 0.5% and such low pH is desirable for creating unfavourable conditions for microbial activity and hence increases the shelf life of the product while maintaining the quality of the canned product.

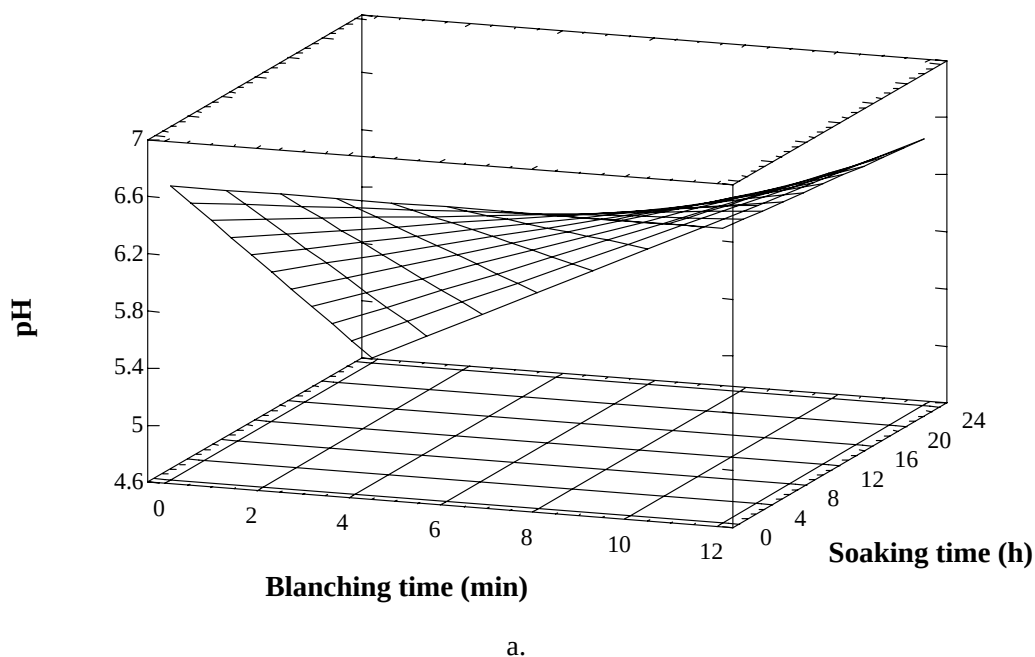


Figure 5. Continued on next page.

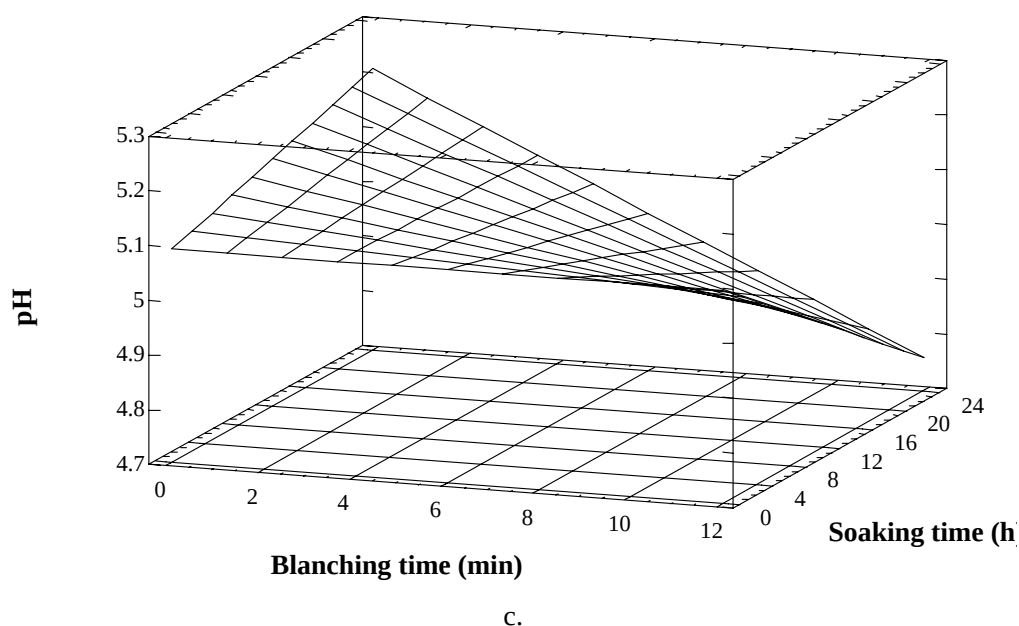
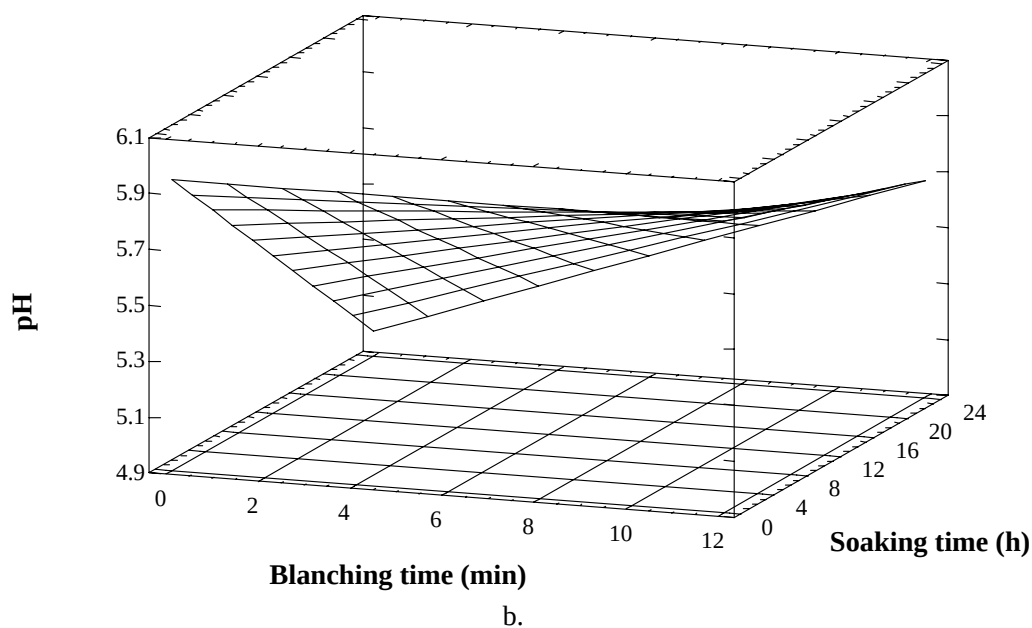
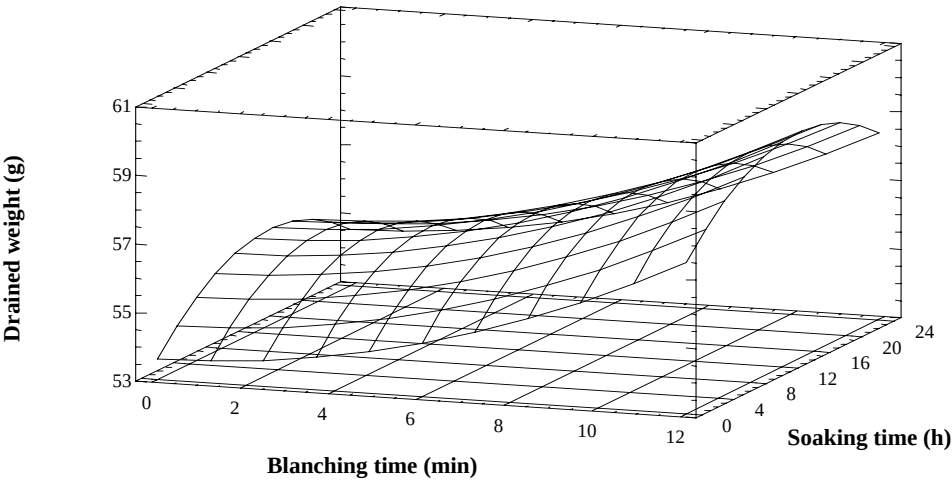


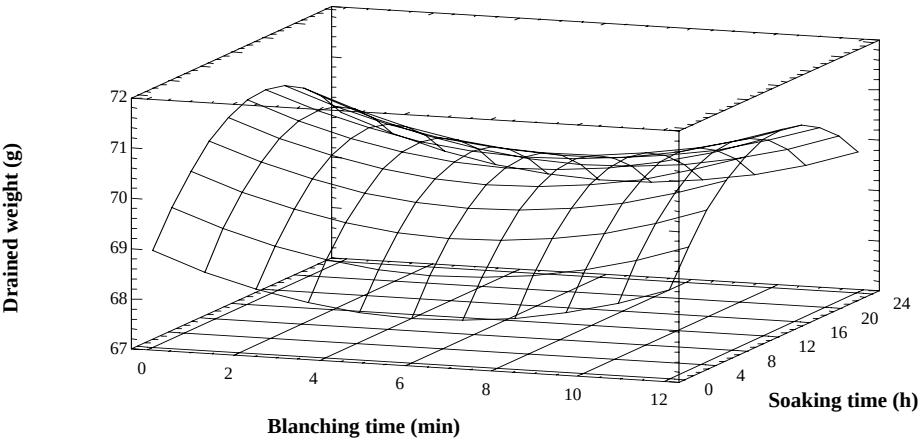
Figure 5. pH of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

Effect of Pre-process Variables on Drained Weight of the Canned Cowpeas

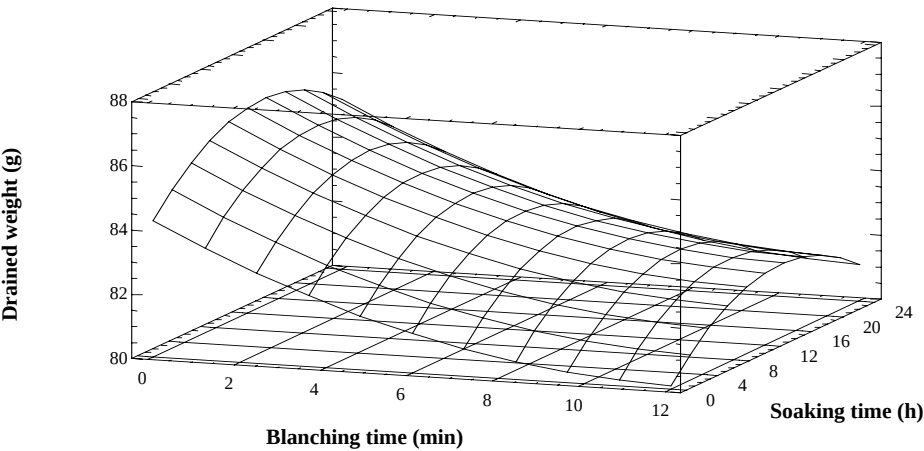
The regression model obtained for drained weight when the IT87D195Y cowpea was used for the canning was: $Z = 53.601654 + 0.31378X_2 + 30.6495X_3 - 0.66225X_1X_3 + 0.02646X_1^2 - 0.01126X_2^2 - 0.01126X_3^2$, with an R^2 of 81.8%. There was a strong and significant



a.



b.



c.

Figure 6. Drained weight of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

($p \leq 0.05$) influence of both the quadratic and linear factors of soaking time. It was observed from the statistical analysis that soaking time had significant ($p \leq 0.05$) quadratic and linear effect on the model. The model could explain about 82.0% of the variations in drained weight. The response plots (Figs. 6a-6c) show that soaking time and blanching time had significant effects on the drain weight of the canned cowpeas. However, increasing salt concentration brought about slight differences in the plot patterns.

The trend was that, the higher the salt concentration, the higher the drained weight. This indicates that the cowpea absorbs more of the salt at higher salt concentration. This is suspected to be resulted from the fact that plant cell in contact with a solution of lower water potential than its own content experiences water leaving its cell by osmosis through the cell membrane, since osmotic gradient cause the movement of molecules or ions from a region of higher concentration (salt solution) to lower concentration. However, with the exception of the product soaked in 1.0% salt concentration which showed decreases in drained weight with increasing blanching time, increasing soaking times led to increasing drained weight in the canned cowpea products (Figs. 6a and 6b). The implication is that canned cowpeas with higher drained weight appear more palatable thereby influencing consumer acceptability.

Effect of Pre-process Variables On splitting of Canned Cowpeas

The model obtained for seed splitting when the IT87D195Y cowpea was used for the canning was: $Z = 5.479413 - 1.60609X_1 + 2.16948X_3 - 0.16385X_2 X_3 + 0.11321X_1^2$, with an R^2 of 78.2%. There was a strong and significant ($p \leq 0.05$) influence of the linear factors of soaking time and $[(NaPO_3)_6]$ and the quadratic factor of blanching time. It was observed from the statistical analysis that soaking time and $[(NaPO_3)_6]$ had significant ($p \leq 0.05$) linear effect on the model, whilst blanching time had quadratic effect. The model could explain about 78.0% of the variations in the splitting level.

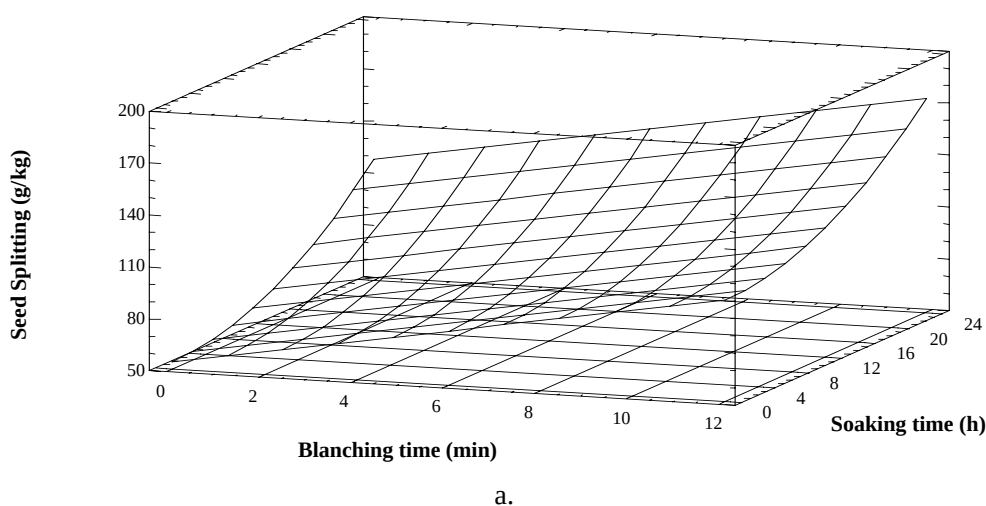


Figure 7. Continued on next page.

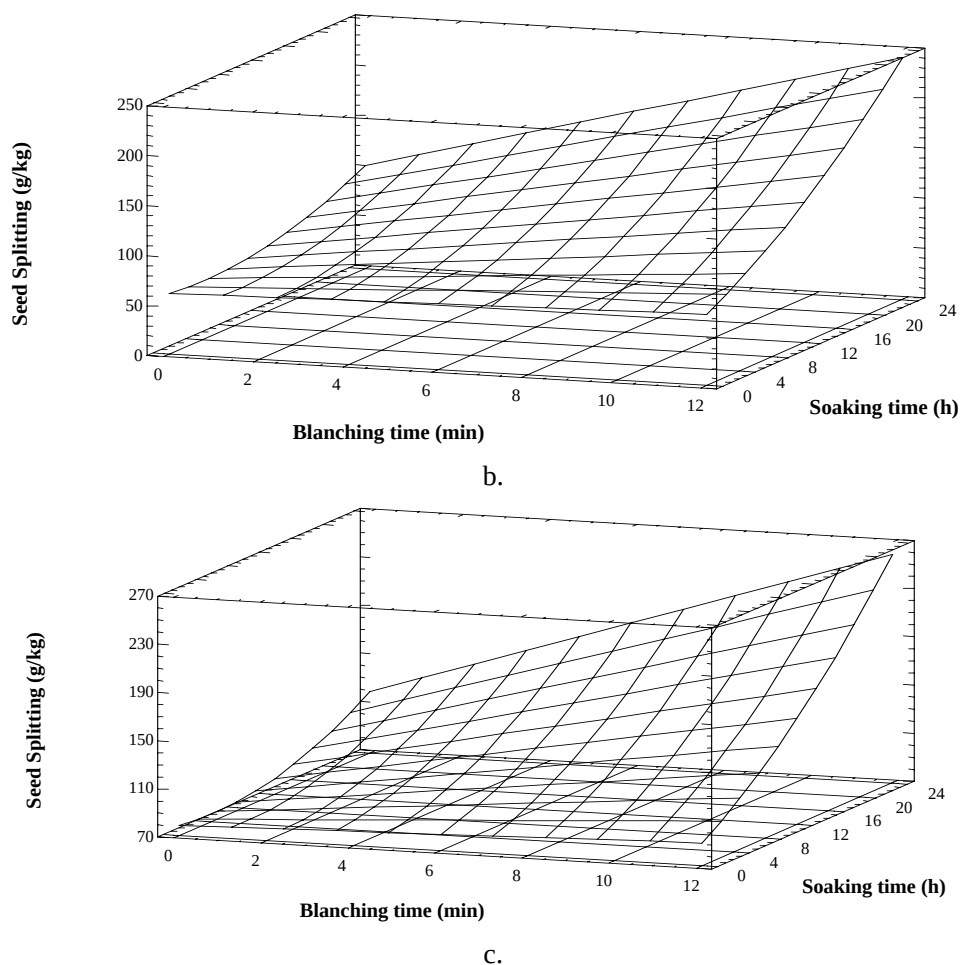


Figure 7. Seed splitting of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

As shown in the response plots (Figs. 7a and 7b), blanching time, soaking time and salt concentration had significant effects on the splitting of the cowpea seeds during the canning operation. Even though the trends were similar, higher salt concentrations led to relatively high seed splitting. Blanching time however had no effect on the splitting of the seeds soaked in 0.5% and 1.0% salt concentrations.

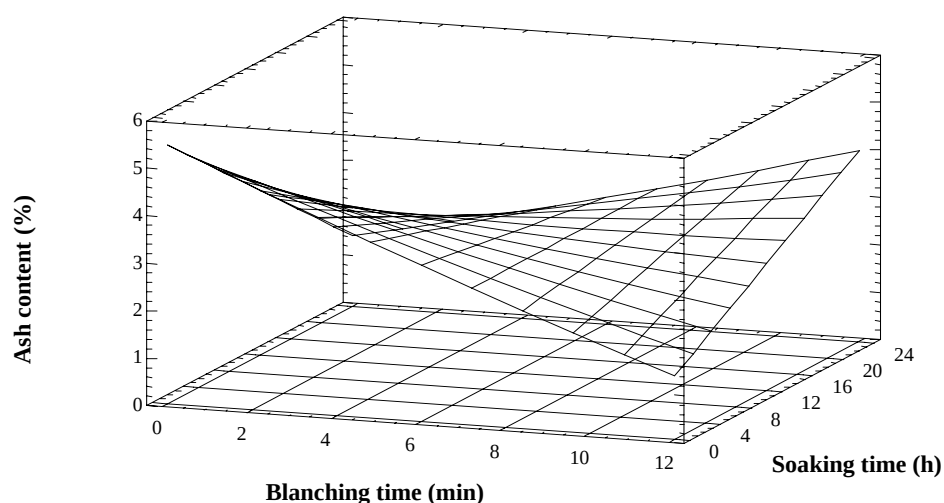
On the contrary, soaking time showed consistent increases in the splitting of the cowpea seeds from the onset of soaking till the end of the soaking period (Figs. 7a – 7c). This agrees with the report by Lopez (1987) that cowpeas are usually soaked for 12 h in water at 180°F to 200°F, and over-soaking causes splitting of the seeds. Canned cowpeas with minimal splitting can increase consumers' preference.

Effect of Pre-process Variables on Ash Content of the Canned Cowpeas

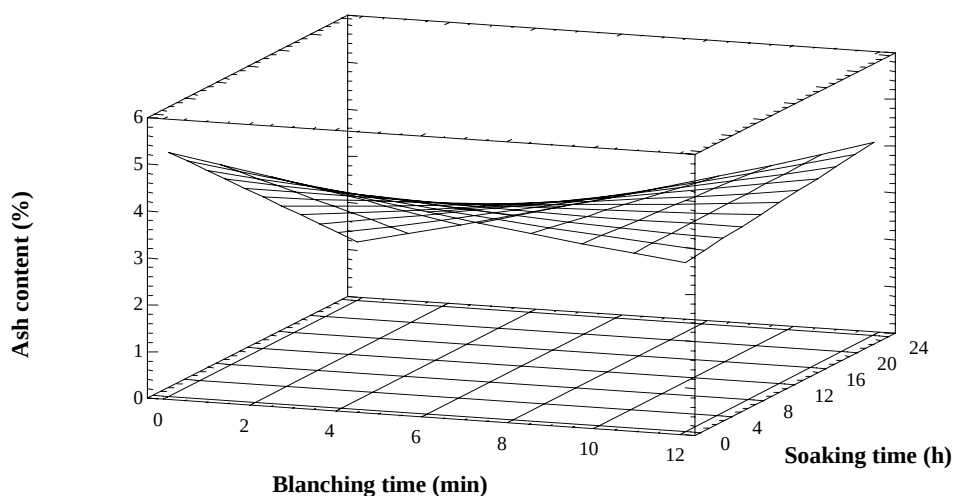
The model obtained for ash content when IT87D195Y variety was: $Z = 5.447071 - 0.37596X_1 - 0.16487X_2 + 0.10423X_3 + 0.02312X_1X_2 + 0.41888X_1X_3 - 0.01523X_1X_2X_3 + 0.00274X_2^2 - 1.13888X_3^2$, with an R^2 of 87.2%. There was a significant ($p \leq 0.05$)

influence of the linear factors of blanching and soaking time for the cowpeas. It was observed from the statistical analysis that soaking time and blanching time had significant ($p \leq 0.05$) linear effect on the model, but no quadratic effect. The model could explain 87.2% of the variations in the ash levels.

The response surface plots generated showed slight increases in ash content with increasing soaking time, with consequential decrease with increasing blanching time of cowpeas soaked with no salt addition (Fig. 8a). However, no observable influences were noted with increasing soaking and blanching times for the seeds soaked with 0.5% and 1% salt concentrations (Figs 8b and 8c). This means that at these concentrations, blanching and soaking did not have any influence on the ash content of the cowpea seeds and therefore the mineral content of the cowpeas are retained.



a.



b.

Figure 8. Continued on next page.

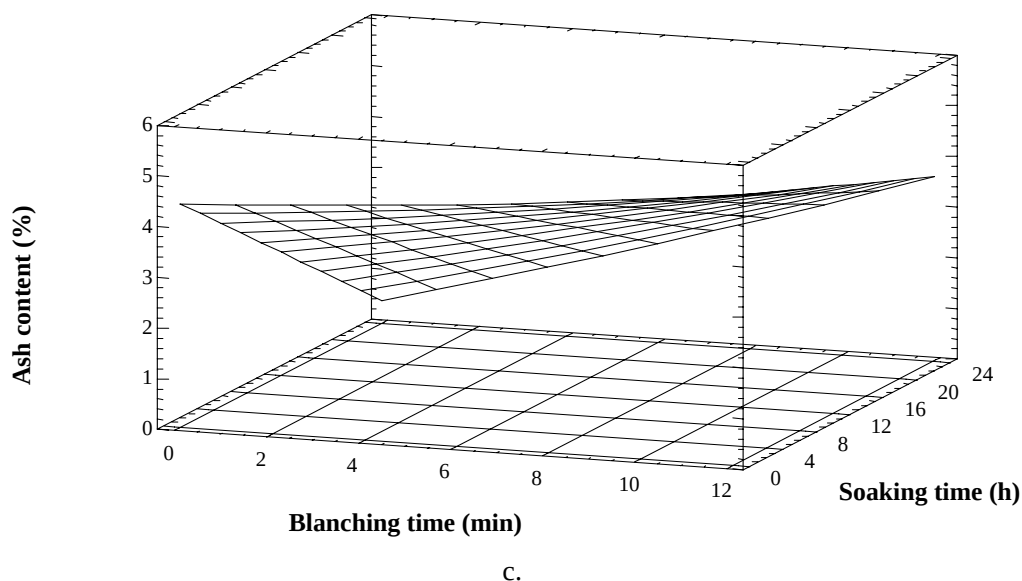


Figure 8. Response surface plot for ash content of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

The ash content of the cowpea soaked in no salt addition was also found to decrease with the increasing blanching time (Fig. 8a). This observation might be due to the fact that during blanching of cowpeas soaked without the sodium salt, some amount of minerals are leached into the blanching medium in the form of leached solids thereby decreasing the ash content of the cowpeas. Lopez (1987) reported that loss of vitamins and minerals during blanching can be significant and is a function of surface area per mass of the product, degree of maturity of the product, type of blanching (hot water or steam), blanching time and method of cooling after blanching (water or air). He further explained that nutrient losses that occur during blanching are caused by leaching, oxidation of water-soluble nutrients and thermal destruction, and that water-soluble vitamins are the most affected. However, the addition of the sodium salt during the soaking caused no reduction in the ash content during blanching (Figs. 8b and 8c), implying that the ash (mineral) content of the cowpeas were retained when the soaking is done with the addition of sodium hexametaphosphate salt.

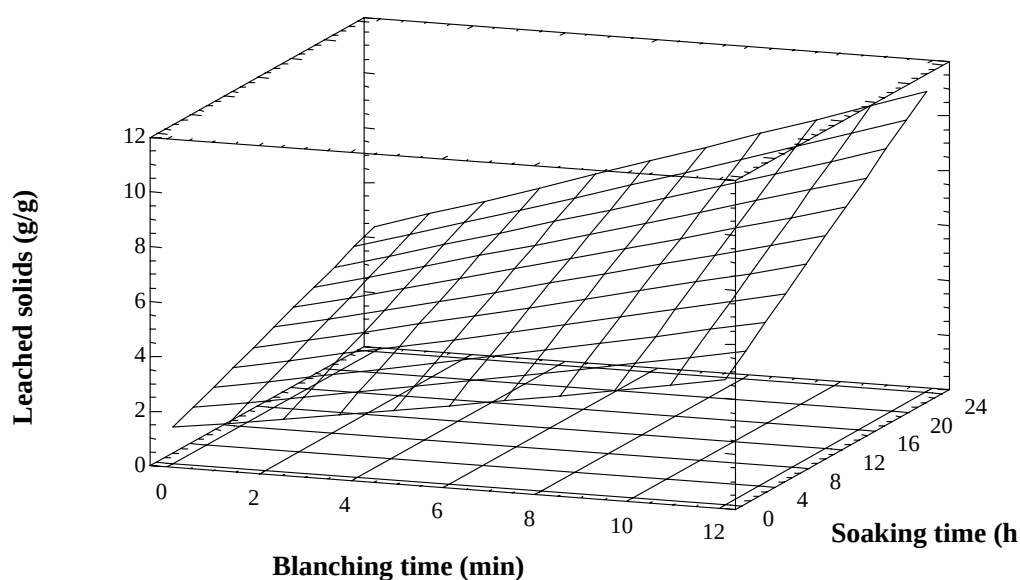
Effect of Pre-process Variables on Leached Solids

The regression model obtained for leached solids when the IT87D195Y cowpea was used for the canning was: $Z = 1.322319 - 0.24665X_1 - 0.12834X_2 - 2.53147X_3 + 0.01121X_1X_2 + 0.28909X_1X_3 + 0.12619X_2X_3 - 0.01726X_1X_2X_3 + 0.00567X_1^2 + 0.00181X_2^2 + 0.45173X_3^2$, with an R^2 of 91.4%. There was a significant ($p \leq 0.05$) influence of the quadratic factor of soaking time. It was observed that soaking time had significant ($p \leq 0.05$) quadratic effect on the model, but no linear effect. The model could explain about 91.0% of the variations in the leached solids.

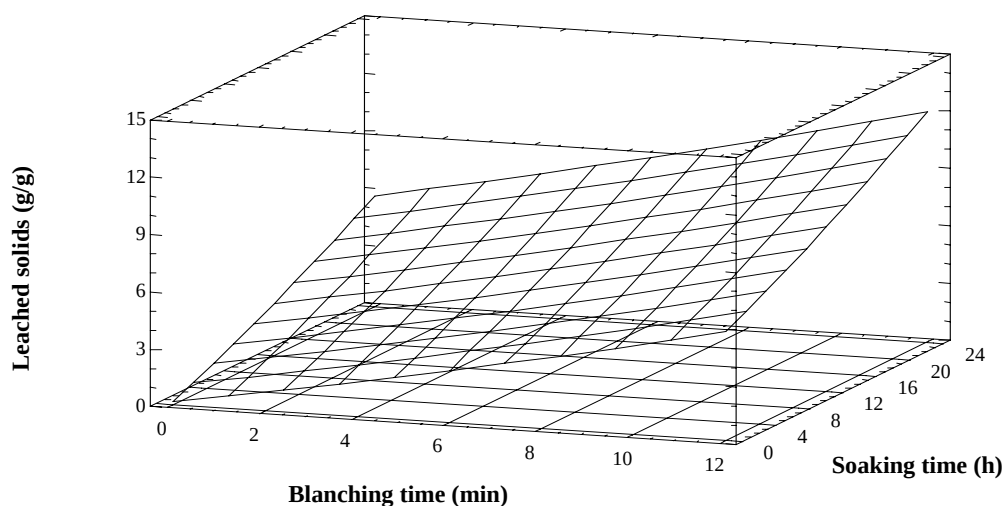
The response plots (Figs. 9a-9c) show that soaking and blanching times had significant effects on the leaching of solids from the cowpea seeds into the soaking medium. The leached solids were found to increase with increasing soaking time and blanching time in all the

different salt concentrations. Phillips (1993) reported that soaking cowpea seeds for 12 h removes 65% of anti-nutrients, which are leached into the soaking water. It is therefore suspected that some dissolved solids were leached from the cowpea seeds when the plant cell comes into contact with a solution of lower water potential for at least 12 h and also when blanched for about 10 min.

Even though the leaching might remove some anti-nutrients from the cowpea seeds prior to canning, too high amount of leached solids can bring about low quality and fast deterioration of the canned cowpeas. Sefa-Dedeh *et al.* (2001) reported that a leached solids of about 8 g/g is enough to cause removal of the anti-nutrients during processing of cowpea seeds with no leaching effect on the nutrients.



a.



b.

Figure 9. Continued on next page.

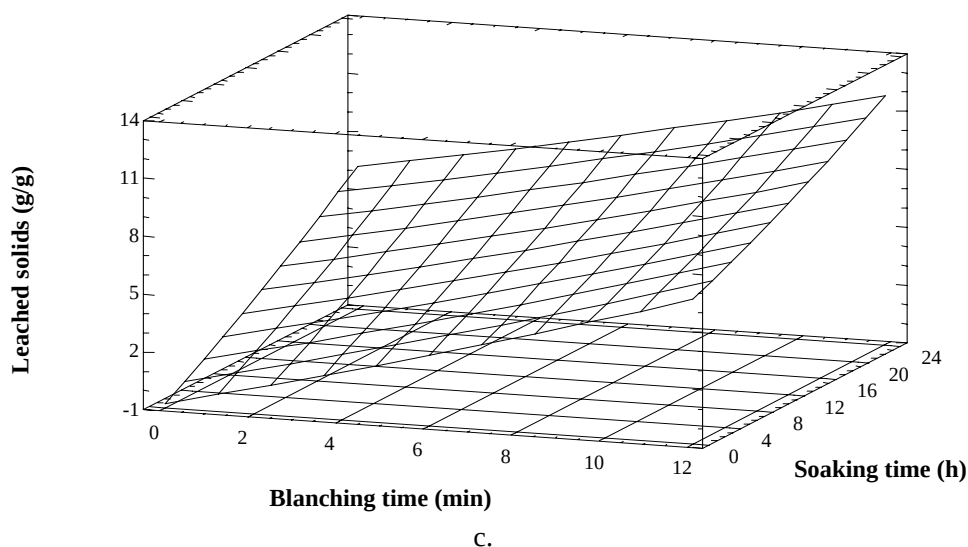


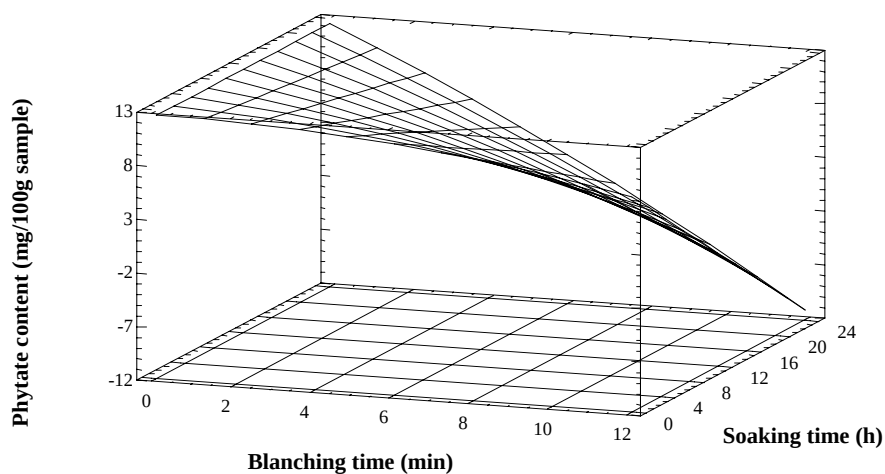
Figure 9. Response surface plot for leached solids of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

Effect of Pre-process Variables on Phytate Content

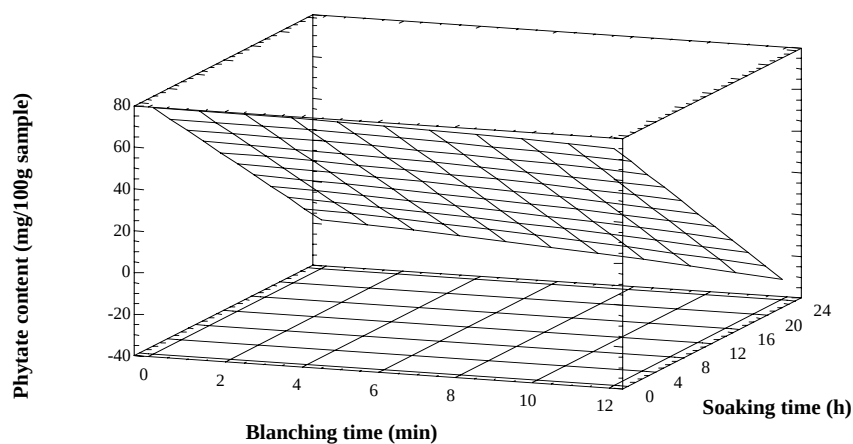
Phytic acid (myoinositol hexaphosphate) is the principal source of phosphorus in dry beans. The interaction of phytate with proteins, vitamins and several minerals is considered to be one of the factors that limit the nutritive value of dry beans (Bressani, 1993). The regression model generated for phytate content when the IT87D195Y cowpea was used for the canning gave a high regression coefficient of 79.5% with a significant lack of fit. The equation generated from the model was: $Z = 12.531266 + 131.2220X_3 + 0.06626X_1X_2 - 9.04057X_1X_3 - 7.89521X_2X_3 + 0.69867X_1X_2X_3 - 0.03099X_1^2$, with an R^2 of 79.5%. There was a strong and significant ($p \leq 0.05$) influence of the linear factors of soaking time, salt concentration $[(NaPO_3)_6]$ and blanching time. Statistical analysis on the data revealed that soaking time, blanching time and salt concentration $[(NaPO_3)_6]$ all had significant ($p \leq 0.05$) linear effect on the model. The model could explain about 80.0% of the variations in the phytate level.

The response surface plots generated (Figs. 10a-10c) showed that the salt concentration and soaking time all had significant effects on the phytate levels of the cowpeas. Increased salt concentration and soaking time resulted in consistent decreases in the phytate contents. Increasing soaking time caused significant decreases in the phytate content, as the anti-nutrients were suspected to be leached into the soaking medium at all the salt concentrations.

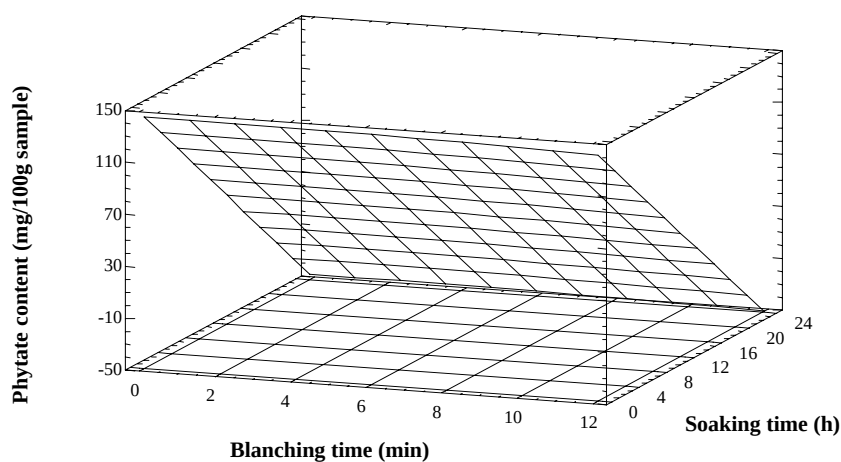
Pearson (1976) reported that soaking cowpea seeds for 18 hours removed 65% of hemagglutinin activity, and soaking mung bean for 24 h at room temperature removed 66% of the trypsin (protease) inhibitor activity, 93% in lentil, 59% in chickpea and 100% in broad bean. In addition, it has been reported that blanching for long time removes most or all of the anti-nutrients in cowpeas seeds (Phillips, 1993). Nutrient losses that occur during blanching are caused by leaching, oxidation of water-soluble nutrients and thermal destruction (Lopez, 1987). The results showed that the soaking cowpea seeds for 12 h in 0.5% salt concentration and blanching for 5 min removed all the phytates in the cowpeas.



a.



b.



c.

Figure 10. Response surface plot for phytate content of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

Effect of Pre-process Variables on Tannin Content of Canned Cowpeas

Tannins are polymers resulting from the condensation of flavan-3-ols and comprises any large polyphenolic compound containing sufficient hydroxylic and other reactive, e.g. carboxylic groups, to form strong complexes with proteins and other macromolecules. As components of food or feed, tannins reduce the biological value of dietary proteins (Bressani, 1993; Eyzaguirre *et al.*, 2006). The regression model obtained for tannin content was: $Z = 5.529647 + 0.03476X_2 - 0.01062X_1X_2 - 0.04044X_2X_3 + 0.01333X_1X_2X_3$, with an R^2 of 72.0%. There was a significant ($p \leq 0.05$) influence on the linear factors of soaking time. Statistical analysis conducted on the data showed that soaking time and blanching time had significant ($p \leq 0.05$) linear effect on the model, but no quadratic effect. The model could explain about 72.0% of the variations in the tannin content.

The response plots (Figs. 11a-11c) showed that increasing soaking time led to drastic decreases in the tannin content of the cowpeas with all the different salt concentrations used.

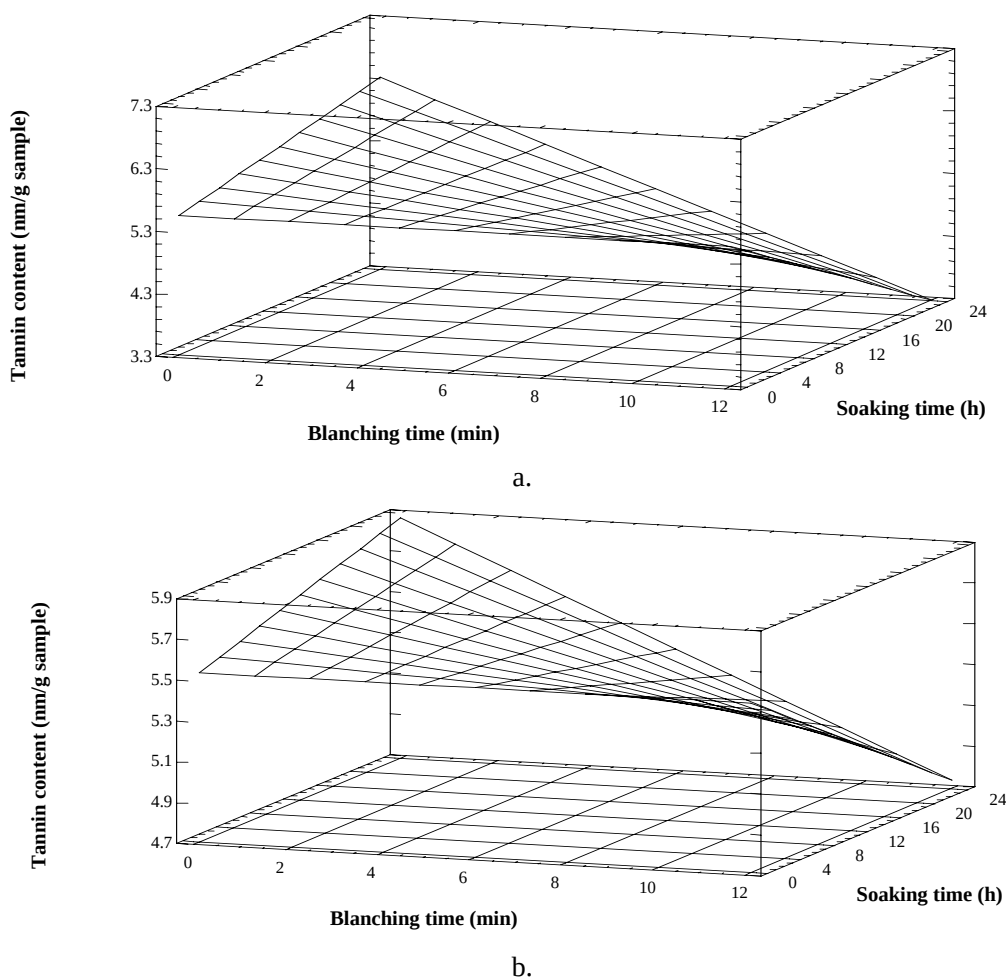


Figure 11. Contineud on next page.

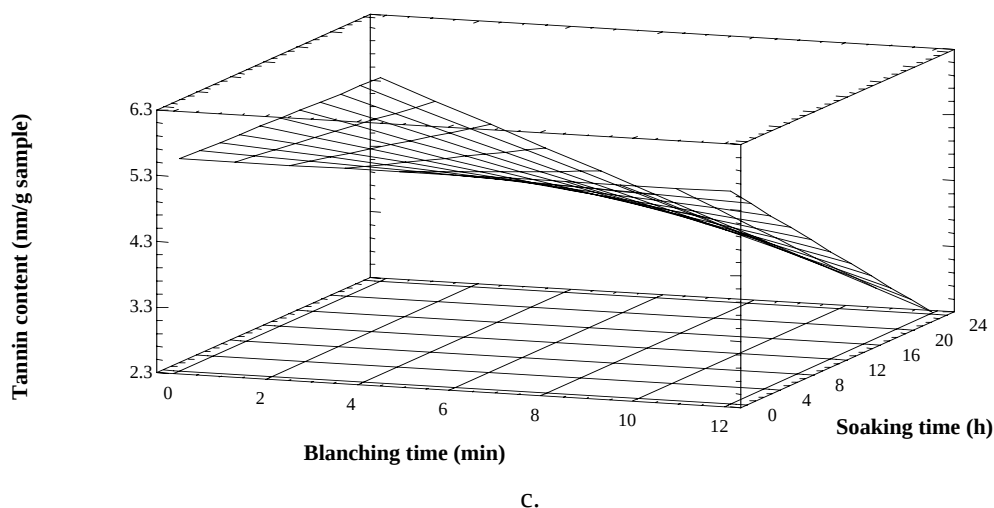


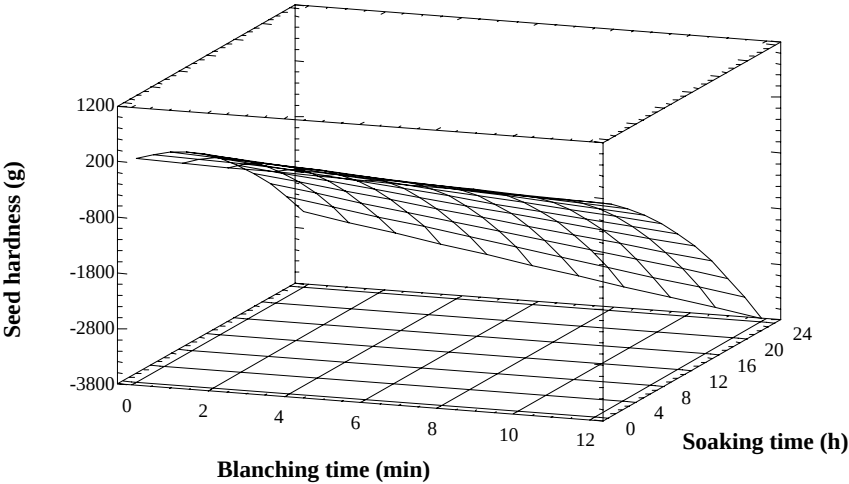
Figure 11. Response surface plot for tannin content of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

This means that soaking cowpea seeds for about 24 h prior to canning can effectively reduce their tannin levels to insignificant amounts, independent on the salt concentration used in the soaking medium. The variation in the salt concentration caused only slight change in the patterns of the plots. Increasing blanching time however caused no effect on the tannin content of the cowpeas indicating that blanching did not influence the tannin levels during canning of cowpeas but some slight reducing effect was noted with salt addition.

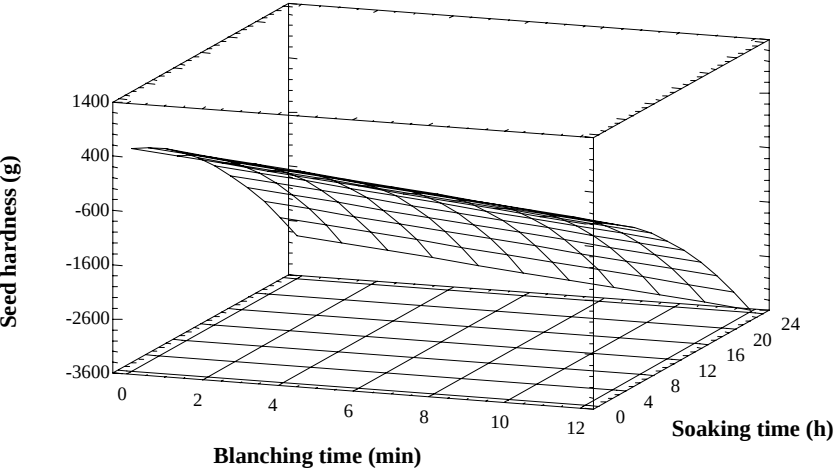
Effect of Pre-process Variables on Hardness (Texture)

The model obtained for hardness of the cowpea was: $Z = 215.618596 + 13.54530X_1 - 30.4813X_2 + 577.9810X_3 - 3.94670X_1X_2 - 102.0100X_1X_3 - 55.1591X_2X_3 + 8.09087X_1X_2X_3 + 3.34582X_1^2 + 32.1208X_3^2$, with an R^2 of 75.8%. There was a strong and significant ($p \leq 0.05$) influence of the quadratic factor of blanching and linear factors of soaking time, salt concentration $[(NaPO_3)_6]$ and blanching time. It was observed from the statistical analysis that soaking time and salt concentration $[(NaPO_3)_6]$ had significant ($p \leq 0.05$) linear effect on the model, whilst blanching time has both quadratic and linear effect. The model could explain about 76.0% of the variations in the hardness level.

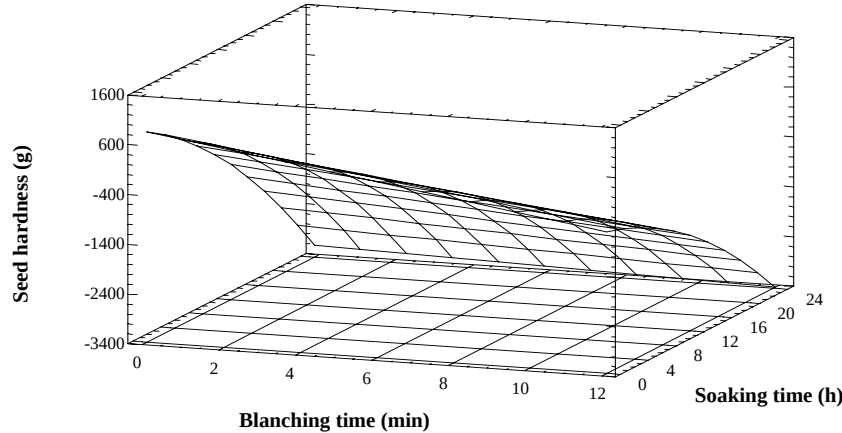
As shown in the response plots (Figs. 12a-12c), all the factors had significant effects on the texture (hardness) of the canned cowpeas. The variations in the salt concentration brought about slight changes in the pattern of the response plots, which is an indication of the fact that increasing the salt concentration influences the hardness of the cowpeas (Figs. 12a-12c). The plots revealed that increasing soaking time resulted in consistent decreases in the hardness of the canned cowpeas.



a.



b.



c.

Figure 12. Response surface plot for heed hardness of the canned cowpea at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

Lopez (1987) noted that cowpeas soaked for longer periods of time tend to become soft. On the other hand, the decrease in hardness as a result of the increasing soaking and blanching times were due to the fact that, there is a disruption of cell integrity as a result of an ion exchange reaction between sodium ions and the divalent ions in the intracellular cement during soaking (Pearson, 1976). Again, if cowpeas remain in water for a long time they become soft (Lopez, 1987). Earlier work by Sefa-Dedeh *et al.* (2001) reported that for acceptable cowpea product formulation, a hardness level of 500 g is ideal. From the study, it was observed that soaking time of 12 hours and $[(\text{NaPO}_3)_6]$ salt concentration of 0.5% with 5 min blanching gave a hardness value of 500 g and effected considerable retention in mineral levels, and drastic reduction in anti-nutrients concentrations. These conditions would therefore be optimal for achieving acceptable product quality characteristics.

Study Two: Canning of Bambara Groundnut (*VOANDZEI SUBTERRANEA*)

Response surface methodology for studying the effect of processing conditions on some quality characteristics of bambara groundnuts (*Voandzei subterranea*) during canning

Study Background

Bambara groundnut (*Voandzea subterranea*) is an African crop, which produces an almost balanced food. It originated in the Sahelian region of present day West Africa, and derived its name from the bambara tribe who now live mainly in Mali. Although considerably less popular throughout the world, cultivation of bambara groundnut has remained common in all of West Africa. It is a drought tolerant and easy-to-cultivate crop, which makes very little demand, if at all, on the soil (Doku, 1996). It serves as an important source of protein in the diets of a large percentage of the population in Africa, particularly to poorer people who cannot afford expensive animal protein, by being among the least expensive, most easily transported non-processed protein sources for both rural and urban dwellers. It is ranked the third most important grain legume after groundnut (*Arachis hypogaea* L.) and cowpea (*Vigna unguiculata*) (Rachie & Silvester, 1977; Baryeh, 2001; Afoakwa *et al.*, 2004).

Nutritionally, most researchers agree that lysine is high, while methionine and calcium are low (Doku, 1996). Studies by Amartefio *et al.* (1997) revealed that it contains 6-12% fat, 14-24% protein and 28-53% carbohydrates, and they make a well-balanced food with a caloric value equal to that of a high-quality cereal grain. Moderate amounts of B-vitamins and small amounts of minerals and vitamins A are reported (FAO, 1988). They can be eaten raw without ill effect, but cooking will destroy the inhibitor and allow the body to make maximum use of the seed protein (FAO, 1988). To make bambara groundnut edible and to increase their shelf life, they are usually dried, processed and preserved by cooking or sterilization of the dry beans to develop acceptable flavour, texture, and inactivate anti-nutritional factors to make the bean's protein nutritionally available to human life. The processing method involves soaking the bambara groundnut in water, draining and cooking or sterilizing in fresh boiling water or brine. Factors such as storage conditions, soaking

treatment and cooking method influence the cookability or sterilisability and acceptability of the bambara groundnuts. In spite of the wide utilization of bambara groundnuts as food in most developing countries, its availability is seasonal and therefore limited to its harvesting season, making it unavailable all year round. Canning of bambara groundnuts is therefore suggested to increase its availability all year round and to provide alternative food processing approaches to the commodity.

Thermal processing is an important method of food preservation in the manufacture of shelf-stable canned foods, and has been the cornerstone of the food processing industry for more than a century. The quality of canned food is dependent on many factors such as retort temperature, can size and shape, thermal properties and other processing parameters. To obtain the best quality product, each combination of processing conditions has to be carefully studied (Chen & Ramaswamy, 2002; Simpson *et al.*, 2006). Some work done on cowpea seeds noted that pre-canned cowpea is usually soaked in cold soft water for 10 to 12 hours, although an occasional lot may require somewhat less soaking depending on the moisture content of the peas and the hardness of the water (Afoakwa *et al.*, 2006; Lopez, 1987). As well, the addition of 0.2% sodium hexametaphosphate has been found to be satisfactory in water having 26 to 29 grains total hardness per gallon. Sodium hexametaphosphate has the general purpose of stabilizing or improving texture. It softens texture of canned peas, beans, meat and poultry. The time of blanching depends on the texture and type of peas being blanched (Lopez, 1987). Over blanching or blanching at too high temperature may cause the peas to split their skins. However, some canners have been successful in packing cowpeas by giving them a short soak (2 to 4 hours), followed by a somewhat longer blanch (10 to 15 minutes). With some types of peas, this long blanch procedure seems to give firmer and less mushy peas, and this procedure requires very careful control of soaking and blanching times, temperatures and careful checking of filling weights. As bambara groundnuts can be suitable for canning like cowpeas, it is important to study the processing conditions that would yield the best quality canned products from them and how these processing conditions affect the nutritional and textural properties of the canned beans.

Response Surface Methodology (RSM) is a collection of mathematical and statistical techniques that are useful for the modelling and analysis of problems in which a response of interest is influenced by several variables with the objective of optimising the response. RSM has important application in the design, development and formulation of new products, as well as in the improvement of existing product design. It defines the effect of the independent variables, alone or in combination, on the processes. In addition to analyzing the effects of the independent variables, this experimental methodology generates a mathematical model which describes the chemical or biochemical processes (Myers & Montgomery, 1995; Anjum, *et al.*, 1997; Afoakwa *et al.*, 2002; Sefa-Dedeh *et al.*, 2003). This work was therefore aimed at employing the techniques of response surface methodology to study the effects of soaking, blanching and sodium hexametaphosphate $[(\text{NaPO}_3)_6]$ salt concentration on some biochemical and textural properties of bambara groundnut (*Voandzei subterranea*) during canning.

Materials and Methods

Materials

Bambara groundnut seeds (*Voandzei subterranea*) was obtained from the Crop Research Institute of the Council for Scientific and Industrial Research (CSIR) of Ghana and used for the study.

Experimental Design for Response Surface Methodology

A Central Composite Rotatable Design (CCRD) of the experiment was set up using Statgraphics software with experimental study variable number $K = 3$, for independent variables including blanching time (X_1), soaking time (X_2) and sodium hexametaphosphate concentration (X_3). The process variables to be used in the CCRD for $K = 3$ could be processed using the software. This will indicate the dependent variable limits and their values. The dependent variables studied included the following: moisture content of the canned bambara groundnuts, ash content, pH of the drained liquid, drain weight of the canned product, leached solids, seed splitting, phytates, tannin content of canned product and hardness (texture) of canned bambara groundnuts.

Twenty sample combinations were generated from the software in experimental design using the design matrix and variable combinations in experimental runs as shown on Tables 2 and 3 above. The bambara groundnuts were canned using tin cans with dimensions of 44.0 mm x 83.7 mm. The pre-processing conditions as indicated in the various combinations generated in the experimental design were conducted on the bambara groundnuts and canned in a still vertical retort at 121 °C (250 °F) for 30 min. The data collated from the experiments conducted on the various combinations were then tabulated accordingly and analysed using stepwise regression analysis.

The Optimisation Process

A stepwise multiple regression analyses was conducted on the data from the Central Composite Rotatable Design to relate blanching time, soaking time and sodium hexametaphosphate (salt) concentration, $[(NaPO_3)_6]$ to moisture content, ash content, leached solids, phytates, tannin content and hardness of the canned bambara groundnuts. The response surface models were generated and presented as 3- dimensional plots in the function of 2 factors (blanching time and soaking time) whilst the salt concentration $[(NaPO_3)_6]$ is kept constant. Adequacy of the model equation for predicting optimum response values was tested in the experiment using the blanching time of 0-12 minutes, soaking time of 0-24 hours and salt concentration $[(NaPO_3)_6]$ of 0-1%. Three optimal processing conditions of the canning procedures of the bambara groundnuts were determined from the mathematical models. In order to get these optimal values, the first partial derivatives of the regression equations were done according to X_1 , X_2 and X_3 and sorted.

Sample Treatments

Equal amount of bambara groundnut was treated with sodium hexametaphosphate concentrations of 0, 0.2, 0.5, 0.8 and 1%, the cowpeas were then soaked in the sodium hexametaphosphate solution for 0, 5, 12, 19 and 20 h, followed by blanching for 0, 2, 5, 8 and 10 min respectively for each experimental run (Table 2). The samples were then processed in a vertical retort for 30 min at 121°C. The results from the parameters studied on the canned products were then tabulated accordingly and analysed using stepwise regression analysis and the regression equation plotted into response surfaces.

Analytical Methods

The analytical methods used in this study were the same as those outlined in the earlier study on cowpea canning.

Results and Discussion

Effect of Pre-process Variables on Moisture Content

The regression model obtained for moisture content of the canned bambara groundnuts was: $Z = 37.7995 - 0.2492X_1 - 0.7345X_2 - 15.7905X_3 + 0.0086X_1X_1 - 0.0916X_2X_2 + 13.2493X_3X_3 - 0.01189X_1X_2X_3$, with $R^2 = 74.41\%$. There was significant ($p \leq 0.05$) influence of the quadratic factors of soaking time, blanching time and salt concentrations on the moisture content of the canned bambara groundnuts. The model could explain about 74.4% of the variations in the moisture content observed. Thus, 25.6% of the variation was attributed to factors not included in the model.

The response surface plots generated for the canned bambara groundnut showed a curvilinear plot with both soaking and blanching times (Fig. 13). The moisture content of the bambara groundnut was initially low during the first eight hours of soaking and then increased gradually till the end of the twenty four hours of soaking. Observed trend for the blanching time differed slightly in the sense there was slight and insignificant reduction in the moisture content within the first four minutes of blanching, after which the moisture increased consistently till the end of the ten minutes of blanching.

The effects of these two processing parameters on the moisture content of the bambara groundnut showed similar trends in all the different salt concentrations (Fig. 13). This indicates that soaking bambara groundnuts in salt concentrations of 0.5% and 1% results in similar trends in moisture content of the canned product. Further blanching of the seeds for 4 to 10 minutes results in 2-4% increase in the moisture of the canned product, suggesting that the processes of soaking, blanching and sodium salt addition employed during canning of bambara groundnuts do not greatly affect the moisture content of the canned product. Preliminary studies (Unpublished) showed that acceptable moisture level in canned bambara groundnuts should be ca. 38-40%, which from this study could be attained after soaking for 12 h in 0.5% salt concentration and blanched for 6 min.

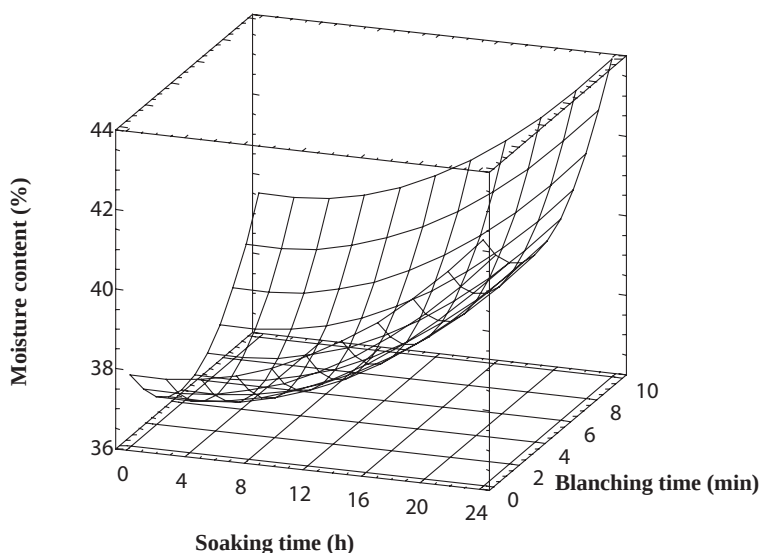


Figure 13. Response surface plot for moisture content of canned bambara groundnut.

Effect of the Pre-process Variables on Mineral (Ash) Content

The model obtained for ash content of the bambara groundnuts was: $Z = 2.3948 + 0.009X_1 + 0.2986X_2 - 0.3497X_3 - 0.00228X_1X_1 - 0.0258X_2X_2 + 0.6008X_3X_3 - 0.0022X_1X_2X_3$, with $R^2 = 66.5\%$. There was a significant ($p \leq 0.05$) influence of the quadratic factor of blanching time and the linear of the soaking time for the canned bambara groundnut. The model could explain about 66.5% of the variation in the ash levels.

The response surface plot generated for the bambara groundnut showed general decreasing trends in the ash content with increasing soaking time (Fig. 14). The blanching effect on the moisture was however different. Blanching caused the ash content to increase gradually during the first 8 min of blanching and then decreased again upon increasing blanching to 10 min. The effect of the salt concentration on the ash content of the bambara groundnuts was not wide enough to cause any significance change.

The decreasing trend noted in ash content during soaking could be due to leaching of minerals from the seeds into the soaking medium with the subsequent uptake of moisture into the seed cells. The combined effect of soaking and blanching however triggered sharp and consistent decreases in the ash content of the product, attributable to loss of leached solids as a result of the susceptibility of minerals to destruction by temperature of the blanching medium as well as the duration of the blanching period. This analogy is supported by Lopez (1987) who reported that loss of vitamins and minerals during blanching can be significant and is a function of surface area per mass of the product, degree of maturity of the product, type of blanching (hot water or steam), blanching time and method of cooling after blanching (water or air). Also nutrient losses that occur during blanching are caused by leaching, oxidation of water-soluble nutrients and thermal destruction, and that water-soluble vitamins are the most affected. Even though there were no variations in the different salt concentrations, it would be economical for industrial purposes to use the sodium salt at 0.5%

concentration. That notwithstanding, the mineral loss in the product was very low when soaked for 12 h and blanched for 6 min, indicating high mineral retention at these processing conditions. Further processing caused drastic reduction in mineral content of the canned products.

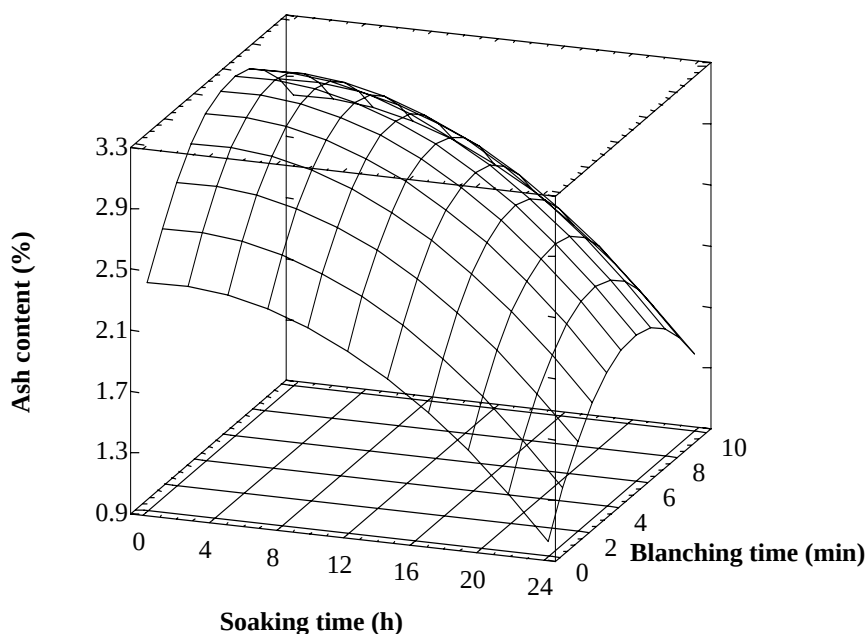


Figure 14. Response surface plot for ash content of the canned bambara groundnut.

Effect of Pre-process Variables on pH

The model obtained for pH when the bambara groundnut seeds were used for the canning was; $Z = 6.0494 - 0.0502X_1 - 0.0464X_2 + 0.7922X_3 + 0.0019X_1X_1 - 0.0046X_2X_2 - 0.7492X_3X_3 + 0.0046X_1X_2X_3$, with $R^2 = 71.0\%$. There were significant ($p \leq 0.05$) influence of the quadratic factors of soaking time and blanching time and linear factor of salt concentration on the pH of the seeds and the model could explain about 71.0% of the variations in pH. The response surface plots developed (Fig. 15) indicated that with the exception of blanching, soaking and salt concentration did not have significant effect ($p < 0.05$) on the pH of the canned bambara groundnut. It was noticed that changes on salt concentration from 0 % to 1 % slightly influenced the pattern of the pH with soaking time and blanching time.

The effect of soaking time and blanching time was quadratic in nature whereas that for salt concentration was linear. There was no observable change in the pH of the canned product from the beginning to the end of the soaking time. For the blanching period, there was an initial slight increase in pH, which was further followed by a rapid decline in the pH of the canned bambara groundnuts from pH of 6 to 2 during the 10 min of blanching. No changes were noted with the two parameters (soaking time and blanching time) with variations in salt concentration (Fig. 15).

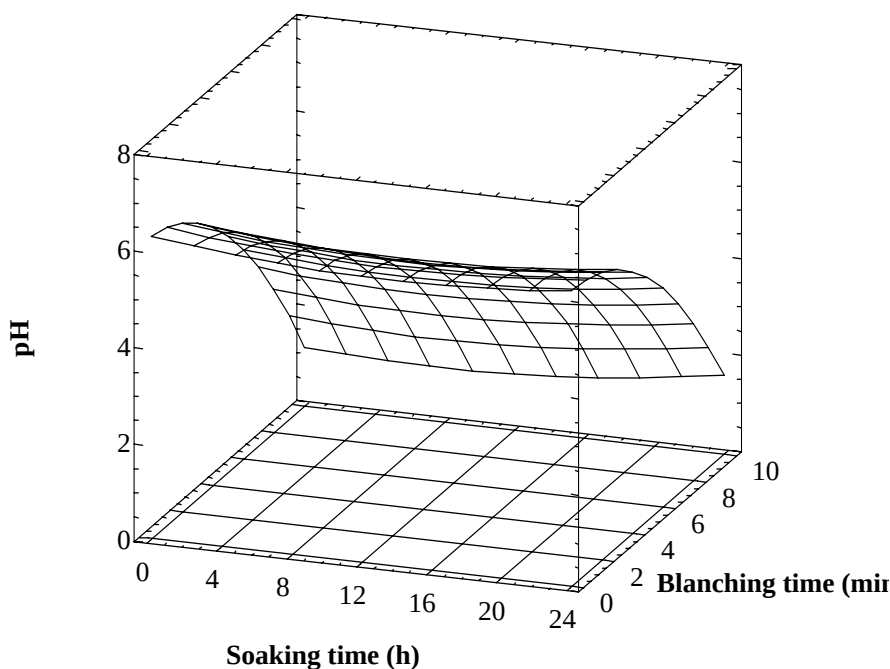


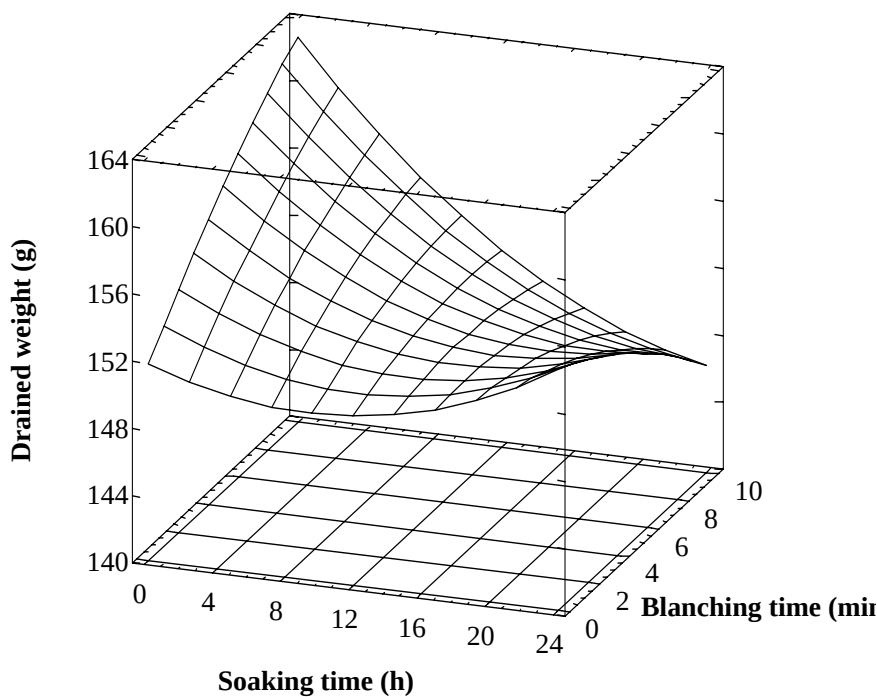
Figure 15. pH of the canned bambara groundnut.

The results revealed that the optimal conditions required to achieve the lowest pH of the canned bambara groundnut were as follows; soaking time of 12 h, blanching time of 6 - 10 min and salt concentration of 0-1%. Blanching for 6 - 10 min created an acidic condition for the seeds, enhancing its storage ability. Generally, lower pH is desirable for creating unfavourable environment for microbial activity and hence increases the shelf life of the canned product.

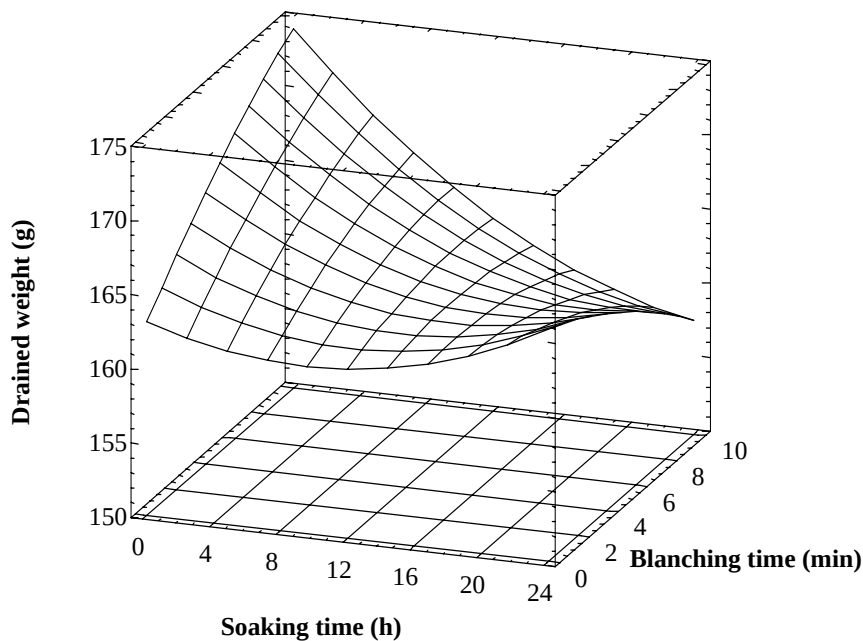
Effect of Pre-process Variables on Drained Weight

The model obtained when the bambara groundnuts was used for the canning was; $Z = 143.9063 - 0.3822X_1 + 1.4636X_2 + 12.0709X_3 + 0.0204X_1X_2 - 0.03404X_1X_3 + 7.0278X_2X_3 - 0.1597X_1X_2X_3$, with an $R^2 = 67.4\%$.

There was a significant ($p \leq 0.05$) influence of both the quadratic and linear factors of soaking time and blanching time and the linear factor of salt concentration on the drained weight of the canned bambara groundnuts. It was also observed from the statistical analysis that soaking time had significant ($p \leq 0.05$) quadratic and linear effect on the model. The model could explain about 67.4 % of the variations in drained weight. Thus, 32.6 % of the variation was due to other factors not included in the model. It was observed that at all salt concentrations (0 - 1%), the drained weight of the canned beans behaved similarly with soaking and blanching times (Fig. 16).



a.



b.

Figure 16. Drained weight of the canned bambara groundnut at (a) 0 and (b) 0.5 - 1% salt concentration.

Products soaked for up to 12 min showed consistent increases in drained weight with blanching time, with no significant changes observed with those soaked for 12 to 24 h at all blanching times. At salt concentrations of 0.5% and 1%, slight increases in the drained weight

of the canned product in terms of soaking time and blanching time were noted but insignificant, and no observed peak value was noted for these two indices at these salt concentrations (Fig. 16b). This trend in drained weight could be due to the fact that higher salt concentration leads to higher drained weight and this gives an indication that bambara groundnut absorb more salt at higher salt concentrations. This is suspected to have resulted from the fact that the plant cells in contact with a solution of lower water potential than its own content, experiences water leaving its cell by osmosis through the cell membrane, since osmotic gradient cause the movement of molecules or ions from a region of higher concentration (salt solution) to lower concentration.

Effect of the Pre-process Variables on Percent Splitting

The model obtained for the percent splitting when the bambara groundnuts was used for the canning was; $Z = 4.5384 - 0.5262X_1 + 0.2356X_2 + 0.5275X_3 + 0.0186X_1X_1 - 0.0348X_2X_2 + 0.0209X_3X_3 + 0.0041X_1X_2X_3$, with an $R^2 = 63.6\%$. There was a strong and significant ($p \leq 0.05$) influence of the quadratic factors of soaking time and blanching time. Thus, the statistical analysis revealed that soaking time and blanching time had significant ($p \leq 0.05$) quadratic effect on the model with no linear effect. The model could explain about 63.6 % of the variations in the splitting level of the canned bambara groundnuts.

The response surface plots showed that soaking time had significant decreasing effect on the splitting of the seeds (Fig. 17). However, no remarkable changes were noted in the seed splitting with blanching time.

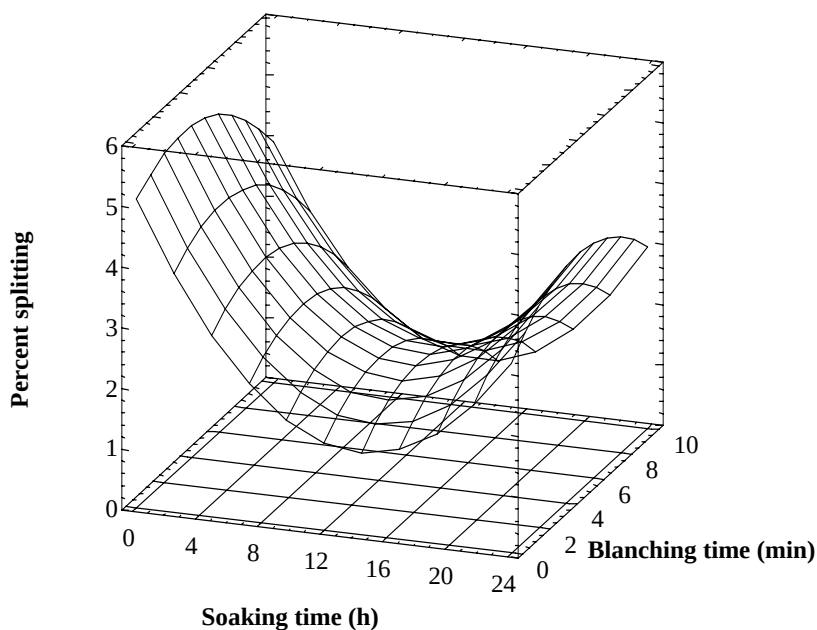


Figure 17. Seed splitting of the canned bambara groundnut at all salt concentrations.

The response plots showed that percent splitting of the seeds decreased significantly within the first 12 h of soaking and thereafter increased further till the end of the soaking time

at all blanching times (Fig. 17), suggesting that soaking bambara groundnuts for 12 h in water gives the lowest splitting effect. Also, differences in the salt concentrations from 0 % to 1 % resulted in similar patterns in the response plots. Further deductions from these observations is that splitting of bambara groundnut seeds during canning depends on the extent of soaking of the seeds in water with or without the salt. Blanching bambara groundnut seeds for up to 10 min prior to canning had only slight and insignificant effect ($p < 0.05$) on the degree of seed splitting.

Effect of Pre-process Variables on Leached Solids

The model obtained for the leached solids of the canned bambara groundnut was; $Z = 0.6771 + 0.011X_1 - 0.00793X_2 - 0.5091X_3 + 0.0005X_1X_1 + 0.0092X_2X_2 + 0.4206X_3X_3 + 0.001X_1X_2X_3$, with an $R^2 = 82.6\%$

There was a strong significant ($p \leq 0.05$) influence of the quadratic factors of soaking time, blanching time and salt concentration, with significant ($p \leq 0.05$) quadratic effect on the model, but no linear effect. The model could explain about 82.6% of the variation in leached solids. Thus, about 17.4% of the variation was due to other factors not included in the model.

The response surface plots (Figs. 18a-18c) showed that all three factors (soaking time, blanching time and salt concentration) influenced the leaching of solids from the bambara groundnut seeds into the soaking medium. The plots showed that leached solids was initially low during the first twelve hours of soaking and then increased gradually till the end of the twenty four hour soaking period. Observed trend for the blanching time however, differed slightly as the level of the leached solids reduced slightly during the first four minutes of blanching and then increased consistently till the end of the blanching time (Figs. 18a-18c).

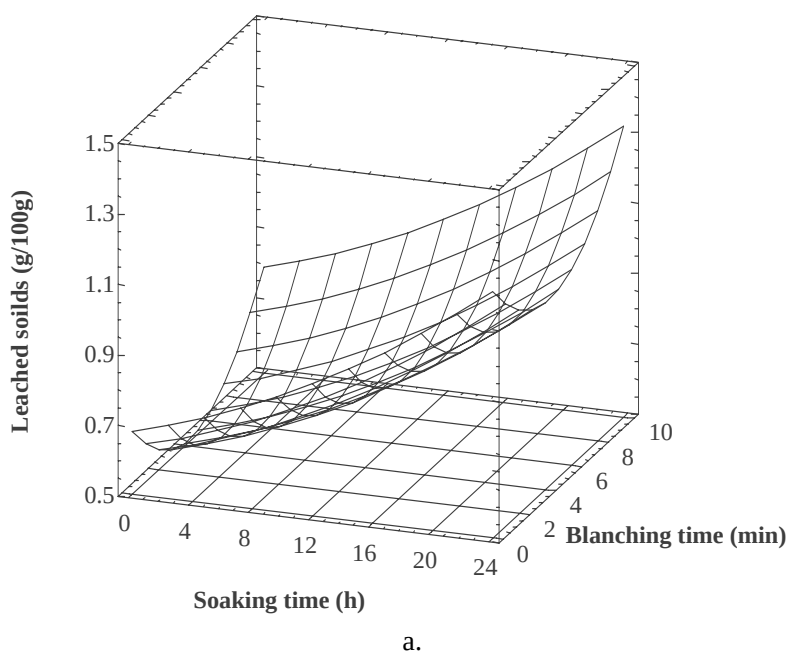


Figure 18. Continued on next page.

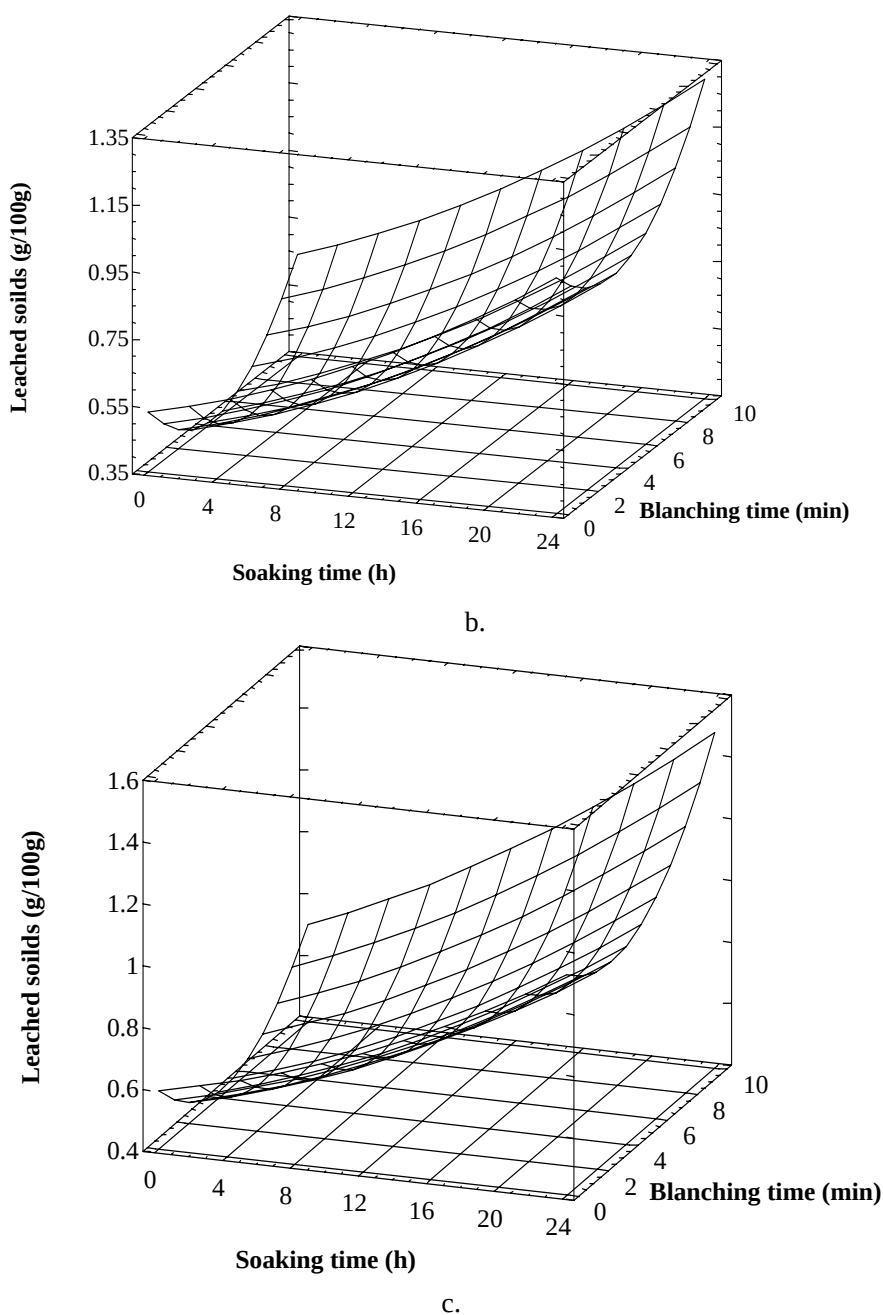


Figure 18. Leached solids of the canned bambara groundnut at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

Peak levels of the combined effects soaking time and blanching time were noted to be highest in seeds canned in salt concentrations of 0 and 1% (Figs. 18a and 18c) and lower in salt concentration of 0.5% (Fig. 18b). Thus, soaking the bambara seeds in 0.5% salt concentration for about 5 min prior to canning can effectively reduce the amount of leached solids of the canned product.

Effect of Pre-process Variables on Phytate Content

Phytates are the principal source of phosphorus in dry beans. The interaction of phytates with proteins, vitamins and several minerals is considered to be one of the factors that limit the nutritive value of dry beans (Afoakwa *et al.*, 2004). Phytates forms complexes with minerals such as Zn and Fe, which lowers their bioavailability and they have been reported to interfere with protein metabolism and decreases the utilization of proteins subjected to proteolytic digestion (Eyzaguirre *et al.*, 2006). The model obtained for the phytate levels of the bambara groundnut was: $Z = 4.91355 + 0.59634X_1 + 5.08527X_2 + 25.78484X_3 + 0.00791X_1X_2 - 0.64431X_1X_3 - 9.95468X_2X_3 + 0.017042X_1X_2X_3$, with an $R^2 = 66.1\%$. There was a significant ($p \leq 0.05$) influence of the linear factors of soaking time and salt concentration and the quadratic factor of blanching time. The model could explain about 66.1% of the variations in phytate levels of the canned bambara groundnut. The response surface plot (Fig. 19) indicates that all the three factors (soaking time, blanching time) had significant effects on the phytate level of the canned bambara groundnut.

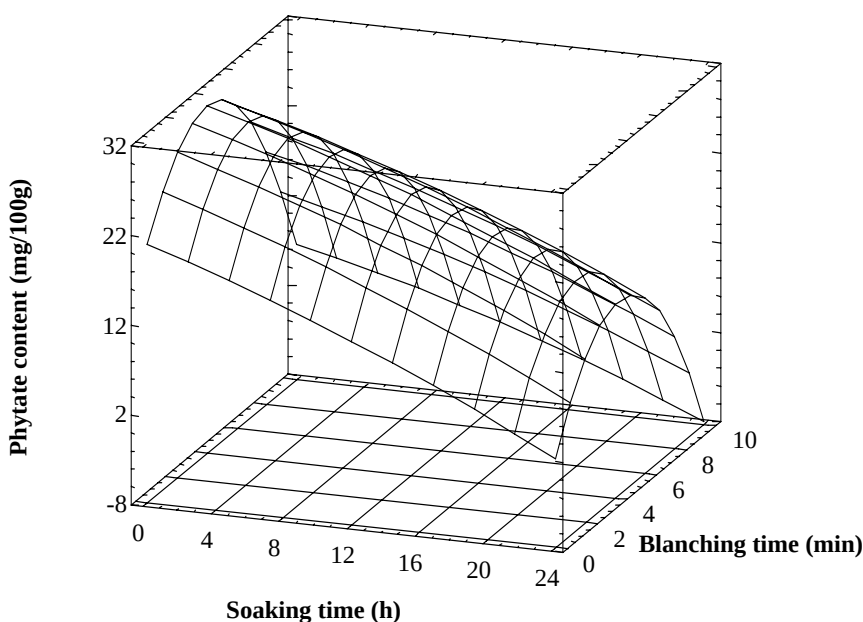


Figure 19. Response surface plot for phytate content of the canned bambara groundnut.

There was sharp and consistent decrease in the phytate levels of the canned product from the beginning to the end of the soaking period. For the blanching period, there was an initial increase in the phytate level, and this was further followed by a rapid decline in phytate level of the canned bambara groundnuts on completion of the blanching time. Salt concentration did not have much influence on the phytate levels.

Phytates are affected by heating and soaking under optimal conditions (55°C, pH 4.5-5.0) can reduce or eliminate phytates (Sardberg & Svarberg, 1991; Hurrell, 1997). This confirms the observation that the combined effects of soaking and blanching after 6 min greatly reduced the level of phytates present in the canned bambara groundnuts to insignificant

levels. However, that effect is not pronounced if the soaked seeds are blanched for less than 6 min. The influence of increasing salt concentrations resulted in a slight and insignificant ($p \leq 0.05$) increase in the phytate levels of the canned bambara groundnuts. An important factor in the precipitation of phytate as its salts is the synergistic effect of two or more cations, which, when present simultaneously, may act together to increase the quantity of metallic phytate precipitated. the amount of these cations and type present can determine this synergistic effect (NAS, 1979).

Effect of Pre-process Variables on Tannin Content

Tannins are naturally occurring compounds in legume seeds, that contain sufficiently large number of phenolic hydroxyl or other suitable groups to enable it form effective cross-links proteins and other macro molecules. As components of food, tannins reduce the biological value of dietary proteins (NAS, 1979; Eyzaguirre *et al.*, 2006). The model obtained for the tannin content of the bambara groundnut was: $Z = 6.31355 - 0.100784X_1 + 0.506214X_2 - 0.10987X_3 + 0.00243X_1X_2 - 0.07601X_1X_3 + 0.02156X_2X_3 + 0.00489X_1X_2X_3$, with an $R^2 = 65.2\%$. There was a significant ($p \leq 0.05$) influence of the quadratic factor of blanching time and linear factors of soaking time and salt concentration. The model could explain about 65.2% of the variations in tannin content of the canned bambara groundnuts.

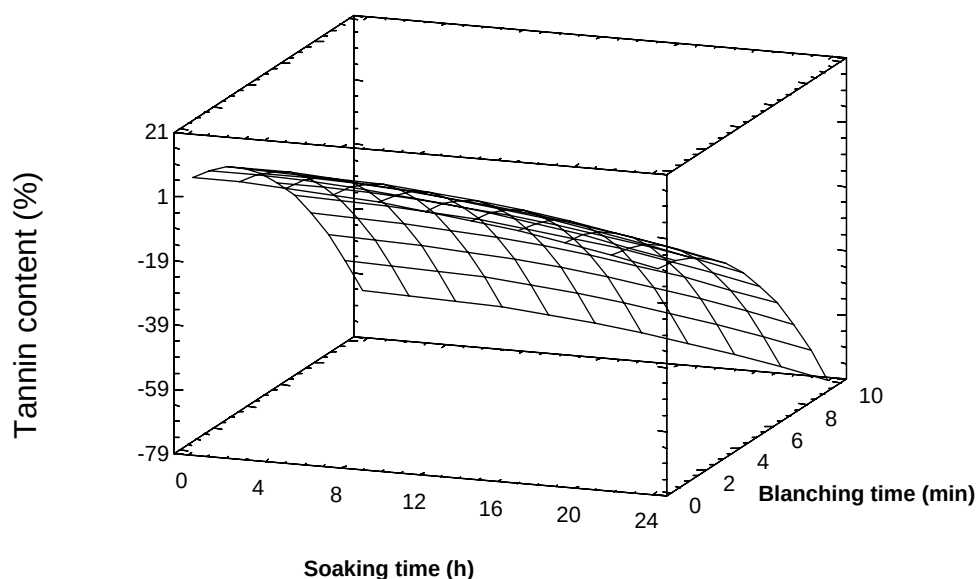


Figure 20. Response surface plot for tannin content of the canned bambara groundnut.

The response surface plots developed (Fig. 20) indicated that soaking time and blanching time had significant effects on the tannin content of the canned bambara groundnut. This trend could be explained that soaking time of 12 hours and blanching time of between 8 and 10 min prior to canning of bambara groundnuts can effectively be employed to reduce their tannin levels to insignificant amounts, independent on the salt concentration used in the soaking medium.

Effect of Pre-process Variables on Texture (Hardness)

Texture is one of the most important parameters used to assess the quality and acceptability of processed foods. The regression model obtained for hardness of the bambara groundnuts was: $Z = 1398.3056 - 97.0545X_1 - 13.6317X_2 - 495.2921X_3 + 3.2443X_1X_1 + 1.2076X_2X_2 + 289.1576X_3X_3 + 0.0196X_1X_2X_3$, with an $R^2 = 79.2\%$. There was a strong significant ($p \leq 0.05$) influence of the quadratic factor of soaking time and the linear factors of blanching time and salt concentration on the seed hardness of the canned bambara groundnuts. The model could explain about 79.2 % of the variation in the hardness level of the seeds.

The response plots revealed that increasing soaking time resulted in a decrease in the hardness of the canned seeds (Figs. 21a-21c). However, increasing blanching time did not influence the hardness of the seeds. Variation in the salt concentration from 0 to 1% brought about significant changes in the levels of hardness in the response surface plots, which is an indication of the fact that increasing the salt concentration influences the hardness of canned bambara groundnuts (Figs. 21a-21c).

The plots revealed that increasing the salt concentration led to significant decreases in hardness of the canned seeds (Figs. 21a-21c). This is suggested to be due to the fact that there were ion exchanges between the sodium ions and the divalent ions in the intracellular cement of the seeds during soaking with the salt solution leading to reduction in the hardness of the canned seeds (Pearson, 1979). However, the hardness levels of the seeds soaked in 0.5% and 1% salt concentrations were comparable. This means for economic reasons, a salt concentration of 0.5% would be ideal for the production of canned bambara groundnuts with an optimal softness. Preliminary studies (Unpublished) showed that texture (hardness) value

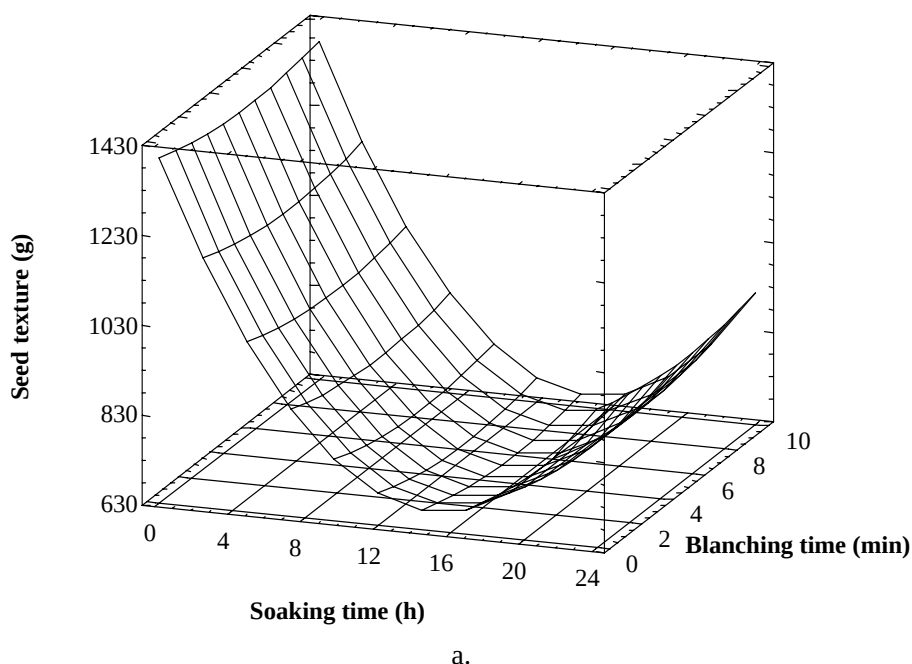
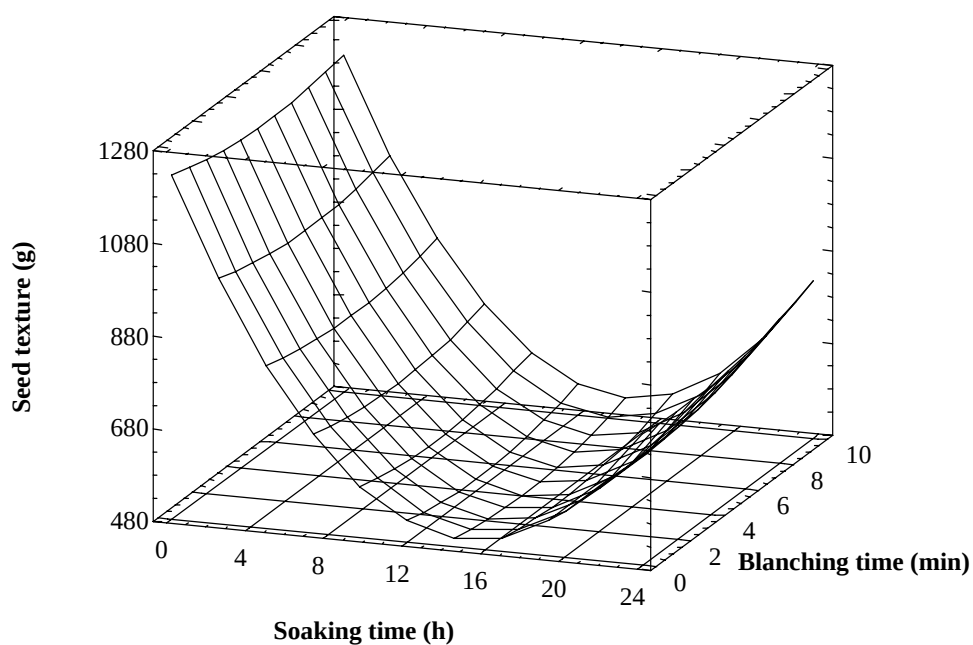
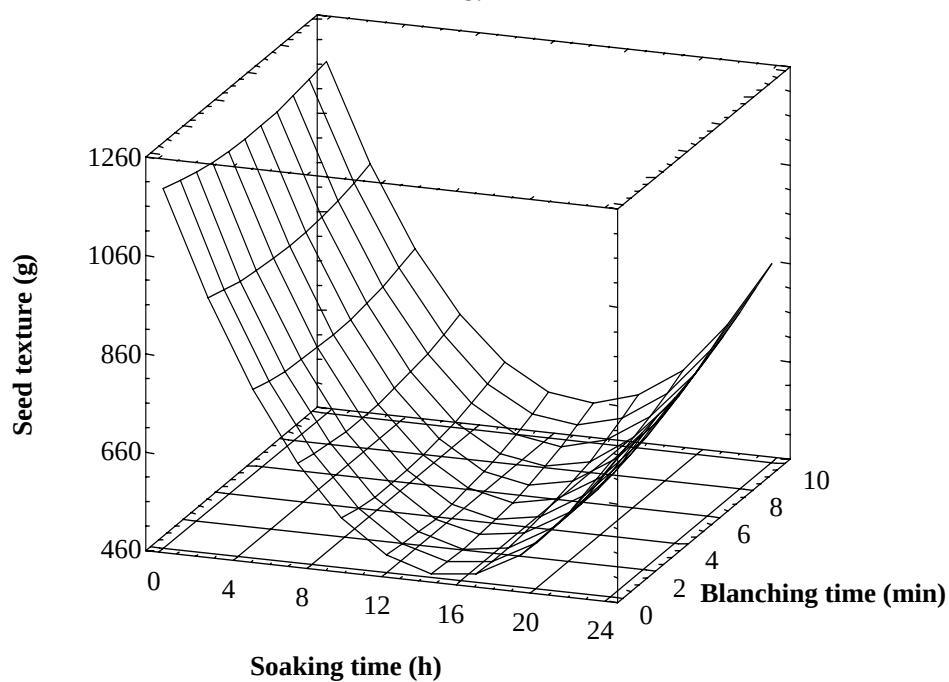


Figure 21. Continued on next page.



b.



c.

Figure 21. Response surface plot for heed hardness of the canned bambara groundnut at (a) 0%, (b) 0.5% & (c) 1% salt concentration.

of 500 g, provides the ideal hardness for consumer acceptability. From the observed trend it can be deduced that the optimal conditions required to achieve the least hardness of canned

bambara groundnuts were; soaking time of 12 h, blanching time of 8 min and salt concentration of 0.5%.

Conclusions

Modelling and optimization techniques using Response Surface Methodology can effectively be used to manipulate canning procedures and their interactions to obtain optimal processing conditions during canning of foods to effect high nutrient retention and enhanced quality characteristics. The two studies showed that blanching, soaking and sodium hexametaphosphate salt concentration all had significant effects on the moisture content, ash content, leached solids, phytates, tannins and the hardness of the canned cowpeas and bambara groundnuts with significant interaction between all the factors. Blanching and soaking prior to canning led to increasing moisture content and leached solids while significant decreases were observed for the phytates, tannins and hardness of the canned cowpeas and bambara groundnut with only minimal losses to the mineral content and leached solids when the seeds are soaked for 12 h. The addition of sodium hexametaphosphate salt during the soaking operation also caused significant improvement (reduction) in the hardness of the seeds achieving optimal texture with 0.5% salt addition. The optimal conditions found to achieve the optimum quality of the canned cowpeas were blanching time of 5 min, soaking time of 12 h and $[(\text{NaPO}_3)_6]$ salt concentration of 0.5%, and for the bambara groundnut; blanching time of 8 min, soaking time of 12 h and $[(\text{NaPO}_3)_6]$ salt concentration of 0.5%. These conditions would give the best quality canned product from both the cowpea and bambara groundnuts with improved nutritional quality and acceptable product quality characteristics, indicating that as recent advances in canning technology, modelling techniques could be employed using RSM to optimize the canning processes to achieve the desired product quality while maintaining their physical and sensory qualities.

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Chapter 7

FUNCTIONAL PROPERTIES OF EXTRUDED FORMULATIONS OF WHEY PROTEIN CONCENTRATE AND CORN STARCH

***S. L. Amaya-Llano^{1,2}, F. Martínez-Bustos¹, L. Ozimek^{3*}
and A. Tecante⁴***

¹Ciencia de Materiales, CINVESTAV Querétaro, Apdo. Postal 1-798,
Querétaro, Qro., 76230, México.

²Posgrado en Alimentos, Universidad Autónoma de Querétaro, Apdo. Postal 184,
Querétaro, Qro. 76010, México.

³Department of Agricultural, Food and Nutritional Science, University of Alberta,
Edmonton, Alberta, Canada T6G 2P5.

⁴Departamento de Alimentos y Biotecnología, Facultad de Química, “E”-UNAM,
Cd. Universitaria, 04510, México, D.F.

Abstract

Starch and proteins processed as individual components offer a wide range of functional properties. Unique blends can be prepared by the extrusion process with a synergistic effect inducing cross-linking sites that contribute to the protein three-dimensional network stability after extrusion, affecting nutritional and functional properties of the new biopolymer to be used in diverse food systems. The aim of this work was to study the effects of extrusion variables such as barrel temperature, feed moisture, alkaline and acidic pH, different proportions of corn starch (CS) and whey protein concentrate (WPC) on protein surface hydrophobicity (S_o), degree of denaturation, rheology, and physicochemical properties of the functional blends. The extrusion variables were barrel temperature (BT 70-180°C), feed moisture (FM 18-30%), pH (3-8) and the ratio of WPC to CS. The physicochemical characterization showed that FM and pH had significant effect on expansion index (EI); EI increased with lower values of FM and higher pH. An interaction of BT and FM had an effect on water absorption index (WAI); at lower FM, the BT effect was nonexistent, whereas at higher BT and higher FM, the WAI increased. PH had a significant effect on WSI, showing

* E-mail address: fmartinez@qro.cinvestav.mx

high WSI when low pH levels were used. Color analysis showed that higher protein content and pH generated color difference values (ΔE); low FM and low pH resulted in gel syneresis. The highest *in vitro* digestibility was obtained when a higher WPC proportion and pH were used. Surface hydrophobicity (S_o) is a good indicator of the hydrophobic side groups available for interactions in food systems. S_o was affected by the extrusion parameters; this information was used to monitor the interaction between proteins and carbohydrates present in the blends. Reversed-phase chromatography was used to evaluate denaturation of protein after extrusion. Although in extrusion denatured protein, S_o values for the blends were lower than those of the individual components. Rheology reinforced these results. The extruded blends of starch-WPC have potential to be utilized in milk-based new food products such as Oaxaca-type cheese analogues and drinking yoghurt-like.

I. Introduction

Starch and protein are two important constituents in food products. The study of starch-protein interaction is of interest to modify or improve the functional properties of starch and protein. However, it is difficult to find a sound example of true starch-protein interaction, and many reported changes in functional properties of starch or protein have been related to water or other food component (Appelqvist and Debet 1997). Traditionally, whey was defined as a byproduct of cheese-making and regarded by cheese producers as waste with little or no commercial value. This view changed radically as increasing numbers of technical and nutritional applications were discovered for whey or whey components, and whey is now considered a coproduct of cheese-making. The composition of whey depends on the method of cheese manufacture. Whey protein concentrates, produced commercially for a number of years, are used to improve both the nutritional protein quality and its concentration of many food products (Walzem et al. 2002). Due to their three-dimensional structures, food proteins are involved in many functional properties. The functional properties of whey proteins are related to their utilization in food fabrication. Whey proteins properties such as emulsification, gelation, water binding, solubilization, whipping/foaming, and viscosity have been reviewed extensively (Kinsella and Whitehead 1989, Korhonen et al. 1998). The food industry is still looking for ways to predict the functional properties of proteins as a function of their processing and/or coprocessing. The structures adopted by a globular protein under a particular set of environmental conditions depend up on a delicate balance of physicochemical phenomena, including hydrophobic interactions, electrostatic interactions, hydrogen bonding, van der Waals forces, and configurational entropy (Mc Clements 2002). Among these factors, hydrophobicity is known to be significantly related to the functional properties of proteins (Alizadeh-Pasdar et al. 2000). Functional properties of WPC are primarily dependent up on the degree of their denaturation and complex formation. Individual whey proteins have different abilities to denature and form aggregates. Hence, the effect of several protein species must be considered when mixed protein systems are heated and then cooled to different temperatures. Processed samples are mixtures of native and denatured proteins, soluble and insoluble aggregates of denatured β -Lactoglobulin (β -LG) cross-linked by disulfide bonds, and complexes of denatured β -LG with α -Lactalbumin (α -LA) and Bovine serumalbumin (BSA). The composition of the processed protein based products is affected by the ratio of whey protein concentrations, the intensity of heat treatment, and the environmental conditions (Moro et al. 2001). Pagliarini et al. (1990) suggested that a variation in surface hydrophobicity is related to heat treatment intensity. They identified that whey

proteins show low surface hydrophobicity values in raw milk because hydrophobic groups are buried inside the native and globular structure of protein molecules, thereby contributing to their orderly structure and stability. If milk is heated at higher temperatures than 70 °C, protein molecules begin to unfold and open hydrophobic sites for interaction. The surface hydrophobicity index increases as the heat treatment becomes increasingly severe. Finally, if the heat treatment is carried out beyond a given time and temperature regime, aggregation phenomena and structural collapse occur, resulting in the decreased surface hydrophobicity of proteins.

II. Raw Materials

Corn starch (CS) and Whey Protein Concentrate 80 (WPC 80) were purchased from IMSA, S.A. (México DF) and America Alimentos, S.A. de C.V., (Zapopan Jal., México), respectively.

III. Methods

The CS-WPC blends were prepared by mixing WPC 80 (25-5%) with CS (75-95%). The pH was adjusted by adding NaOH or HCl (concentration in the range from 0.1 to 1.0 N) and moisture concentration adjusted to the levels indicated in Table 1. The samples were stored in polyethylene bags at 4 °C for subsequent extrusion processing. The extrusion process was carried out using a single screw extruder, designed and manufactured by Cinvestav-IPN, México. The screw compression ratio was 1:1 with a 5.0 mm die-nozzle. The barrel was equipped with electrical cartridge heaters and three independently controlled heating and cooling zones. Barrel temperature in the final zone (zone 3) varied from 70 to 180 °C according to the experimental design (Table 1). The feed rate (73 g/min) and the screw speed (43 rpm) were constant throughout all the experiments. The extrusion variables were: barrel temperature (70-180 °C), feed moisture (18-30%), pH (3-8) and the ratio of whey protein concentrate (WPC) and corn starch (CS). The feed rate of WPC and CS blends varied from 1.74 to 7.06 kg/h and the feed rate depended on the moisture concentration in the blends. Extruded blends were dried to the desired moisture (9.5-10.5%) in a convection oven (40 °C) for 18 h. Depending on the analysis, the final extrudates were used either as a whole or milled in a hammer mill (Pulvex, model 200, Mexico) provided with a 250 µm sieve and packed into polyethylene bags for storage and further analysis. An experimental design of second order without repetitions was used for the extrusion of WPC and CS.

Physicochemical Characterization

Expansion Index (EI)

Dried extruded blends (not milled) were cut into 5 cm pieces for the expansion index (EI) determination, according to the method described by Jin et al. (1994). The expansion index (average) for each extruded product was determined from 20 measurements.

Bulk Density (BD)

The bulk density (BD) was determined using the method of Gujska and Khan (1991). The average diameter and length were measured and the apparent volume (V , m^3) was computed as:

$$V = \left(\frac{\pi \cdot d^2 \cdot l}{4} \right)$$

Where: d (mm) is the average diameter and l (mm) is the length of the extruded product. The bulk density values were calculated from 20 measurements for each product.

Water Absorption and Water Solubility Indexes

Water absorption (WAI) and water solubility (WSI) indexes were registered according to the method of Anderson et al. (1969). Three repetitions were made for each analysis.

Color

Color was measured in extrudates milled to 250 μm . The color was recorded using a Mini Scan Hunter Lab, (Hunter CE96 Associates Laboratory, Reston, VA), following the method of Jin et al. (1994). The color difference for each sample was calculated using the equation:

$$\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$$

Each assay was the average of 20 samples. The blank values were $L = 92.26$, $a = -0.81$, $b = 0.62$.

***In vitro* Digestibility**

In vitro digestibility of protein was measured according to the method of Hsu et al. (1977). Two repetitions were made for each analysis.

Experimental design and data analysis

A factorial design of 16 assays was used in such a way as to allow the main, double interaction and quadratic effects to be estimated. Restrictions in the randomization order of the assays were taken into account in the statistical analysis. All data were analyzed using regression models and Tukey test (Box et al. 1978). The experimental design and its independent variables are shown in Table 1. The statistical analysis was conducted using the Statistical Analysis System (SAS 1996).

Preparation of CS -WPC Gels

Aqueous suspensions of extruded blends (10% w/v) were prepared in a beaker using deionized water. The sample was stirred until homogenization. Oscillatory dynamic

measurements were performed during the heat-induced gel setting, using an ARES-RFS III (TA Instruments, USA), Rheometer equipped with a 25 mm diameter parallel plates; whose temperature was adjusted with a Peltier system (15°C/min). Storage modulus (G'), loss modulus (G'') and loss tangent ($\tan \delta = G''/G'$) were monitored at a fixed frequency depending on sample characteristics and using a 1.0 to 1.5 mm gap. Strain was determined through preliminary strain sweep experiments which targeted linear regions for all conditions employed. Rheology tests were run in duplicate.

Surface Hydrophobicity (S_o) and Denaturation Degree of Proteins

For surface hydrophobicity determination, the powder samples were dissolved in 20mM Tris-HCl Buffer, pH 6.7. The resulting solutions had a protein content of 3.1% (w/v). Solutions were centrifuged 15 min in a Garver Electrifuge for testing milk and cream by Babcock method (Garver Manufacturing Co., Union City Indiana, USA) and 50 μ L of the supernatant were used. Determination of the surface hydrophobicity of the extruded and non-extruded samples was carried out using 1-anilinonaphthalene-8-sulphonate (ANS) as the hydrophobic probe. Aqueous stock solution of hydrophobic probe was 450 μ M ANS (Eastman-Kodak Co., Rochester, NY). Test solutions of 20 μ M ANS in Tris-HCl buffer (pH 6.7) were prepared freshly from the stock solution for the ligand binding study. Stock ANS solutions were kept in air-tight, brown glass bottles. Aliquots (50 μ L) of corn starch-WPC solutions prepared at protein concentration of 31 mg/mL in 20 mM Tris HCl buffer, pH 6.7, were added to 1 mL of 20 μ M ANS. Approximately 10 min after rapid mixing, the relative fluorescence intensity (FI) of milk protein-fluorophore conjugates were measured in a Spectrofluorometer Jasco Model FP6300, STR 313 (Jasco Co., Japan) at room temperature. The wavelengths of excitation (λ_{EX}) and emission (λ_{EM}) were 370 and 480 nm respectively, with slit widths of 5 nm.

The binding data were analyzed according to Closs et al. (1990) and the surface hydrophobicity (S_o) of the CS-WPC solutions was expressed as:

$$S_o = FI / P$$

Where FI is the fluorescence intensity of the protein-fluorophore conjugate, and P is the total protein concentration of the ANS-CS-WPC solution (mg/mL).

Whey protein denaturation was measured by reverse phase high performance liquid chromatography RP-HPLC following the method of Kenelly and Lien (1998), using a Vydac C4 (15mm x 250mm) (Separatius Group, Hesperia, CA). The RP-HPLC system consisted of a binary system. HPLC grade chemicals and Milli-Q water were used throughout the analysis. The buffer systems consisted of buffer A, water-acetonitrile-sodium chloride-formic acid (900:100:10:1 v/v/w/v) and buffer B, water-acetonitrile-sodium chloride-formic acid (600:900:1.5:0.15 v/v/w/v) further filtered and deaerated through a 0.2 mm Millipore filter. Sample solutions (3.1% protein, w/v) were diluted with buffer as in S_o and mixed. Supernatant that contained whey proteins was filtered through a 0.2 mm filter prior to injection into a column. Whey protein standards, obtained from fresh milk were dissolved in buffer A and filtered before injection. Sample injection volume was 50 μ L.

Cheese Analogue

The cheese analogue formulation employed was: 50% water, 20% vegetal fat, 18.8% rennet-casein (82% protein content), 9.2% extruded-milled whey protein-corn starch blend, 0.7% sodium chloride, 0.6% artificial flavor, 0.35% sodium citrate, 0.25% emulsifying salts (Monogrol W, Gardhal, S.A. México) and 0.1% potassium sorbate.

The two analogues that had the best functional profiles were selected and were assessed by sensory evaluation using descriptive and affective methods. In the former case, sensory profiles with 14 descriptors and the participation of 8 trained judges were obtained, and in the latter case acceptance of the products by 93 randomly chosen consumers was evaluated.

Preparation of Yoghurt-Like Drink

Yoghurt-like drink was prepared using the conventional process with *L. delbrueckii* subsp. *bulgaricus* (1.5 w/w) and *S. thermophilus* (0.2 w/w) as starter cultures. Extruded blends were added to yoghurt-like drink formula to replace 50 and 75% of the milk and to achieve a standard of 10% total solids. The sensory panel (6 trained judges) was calibrated to qualify syneresis, color, firmness, flavor, acidity, sweetness, and grainy texture attributes of yoghurt.

IV. Results and Discussion

a. Physicochemical Properties

1. Expansion Index (EI) and Bulk Density (BD)

Statistical analysis showed that feed moisture ($p = 0.0125$) and pH ($p = 0.038$) had the greatest effect in these evaluated responses, and that the protein factor at high barrel temperatures was significant ($p = 0.0384$). All the blends extruded at 180 °C barrel temperature showed the lowest values for EI, ($p < 0.0001$), and the rest of the extruded blends had similar values for EI. Samples extruded at low feed moisture (18%), and barrel temperature (70 °C), alkaline pH (8), and 5% of WPC added to the blends, showed maximum EI values, slightly higher than the samples extruded at barrel temperatures lower than 180 °C. Probably high barrel temperatures increased the amount of fragmented starch and increased protein denaturation leading to formation of insoluble aggregates, thus decreasing EI. Previous findings (Onwulata et al. 1998, 2001, Matthey and Hanna 1997, Fernandez-Gutierrez et al. 2004) had shown that maximum expansion values were found with whey and milk protein concentration < 10%, feed moisture > 25%, pH (6-7) and barrel temperature (125-130 °C). Probably, as reported by Cha et al. (2001), although higher temperature leads to greater vapor pressure and increased driving force for expansion, it may also lead to a decrease in melt viscosity and consequently a greater tendency for the extrudates to collapse. In addition, it is possible to increase gelation, microcoagulation, formation of starch-protein bonds, and affect digestibility. Camire et al. (1990), and Seker (2005), reported that during extrusion there could be a possible protein-starch interaction, decreasing the free expansion of amylopectin chains and inhibiting the release of water content; thus, decreasing expansion and increasing density more easily. In general, the BD values were slightly modified (900-1600 Kg/m³). These results are consistent with the findings reported by Onwulata et al.

(2001). They reported that addition of WPC, whey isolate or casein, did not change the density significantly. In this research, extrudates with high BD developed a dense and rigid structure, probably because under the extrusion conditions tested, the starch was not fully gelatinized and plasticized, thus decreasing EI. Zaleska et al. (2001) reported that potato starch-casein complexes induced by mixing in aqueous solutions and electrosynthesis formed some covalent bonds at lower pH in which the carboxylic groups of protein and the hydroxyl groups of starch are involved. Furthermore, they added that kinetic measurements and analysis of thermogravimetric thermograms suggested a preference for the formation of the starch:casein 1:1 complex. In samples containing a small excess of protein the 1:1 complex co-precipitated with casein.

2. Water Absorption Index (WAI)

Statistical analysis of WAI, showed that the barrel temperature ($p = 0.0007$) factor and its interaction with feed moisture ($p = 0.0010$) were significant; however, feed moisture did not show a significant effect ($p = 0.6455$). At low feed moisture, the effect of barrel temperature was not significant, while at high levels of both factors, the WAI values increased. Thus, the blends extruded at 180 °C barrel temperature, low and high feed moisture and at extreme pH, had the highest WAI values, regardless of the protein content in the blends. WAI values for CS and WPC were 2.128 and 6.320, respectively. Extruded blends increased WAI from 1.5 to 3.5 times more than CS, and in some cases higher than WPC. The high hydration capacity of the blends probably depends mainly on the inter-intra-molecular bonds between WPC and amylose and amylopectin, induced by high barrel temperatures, as well as on the changes that the starch undergoes during extrusion. Similarly, Onwulata et al. (2001) reported that corn products formulated with three different milk proteins (casein, whey protein concentrate (WPC), and WPI added at 25%), increased WAI with WPC, decreased WAI with WPI, while no variation was found with the addition of casein. These functional characteristics of extruded WPC-CS make possible its application in the food industry as a thickening agent and for improving nutritional value (Hudson and Daubert 2002). Similar behavior in WAI of extruded cornmeal-WPC was reported by Kim and Maga (1987). They found an increase in WAI when barrel temperature and feed moisture were increased, and a decrease when WPC was increased in the blends. In addition, increasing casein in extruded blends of casein-wheat starch, increased WAI and decreased WSI (Fernandez-Gutierrez et al. 2004).

3. Water Solubility Index (WSI)

In the WSI, the significant factor was pH ($p = 0.0358$); at low pH values the WAI values were high. According to Onwulata et al. (2003) the degree of extrusion-induced insolubility (denaturation) or texturization, determined by lack of solubility at pH 7, for WPI, increased from 30 to 60, 85, and 95% at 35, 50, 75, and 100°C temperature conditions, respectively. Extruded blends in acidic conditions showed the highest WSI values, increased by low feed moisture; whereas at alkaline conditions, the WAI of the extruded blends was high and the WSI was low. The protein factor was not significant, although associated with pH, and probably as a result of a synergistic effect of both factors; protein denaturation affected the WAI. The level of denaturation and subsequent insolubility depends on the heating temperature and time, and the pH of the whey upon heating (Ennis and Mulvihill 2000). The addition of WPC and WPI to extruded corn starch products decreased solubility values significantly; while addition of casein increased them (Onwulata et al. 2001). Also

Fernandez-Gutierrez et al. (2004) found that increasing the barrel temperature from 126 to 194 °C of casein-starch blends, increased their water solubility index (WSI). Onwulata et al. (2006) reported similar results during extrusion of WPI under acidic and alkaline conditions. These researchers reported that extruded WPI significantly increased solubility in relation to the control (raw WPI), although the highest values for solubility were for the samples extruded under acidic conditions. In addition, these researchers found that the extrusion process was more severe in alkaline conditions than in acidic conditions, as revealed by the high water index values found in alkaline conditions. These differences are probably due to the starch's protective effect against protein denaturation.

4. Color

CS had the highest L value, and WPC the highest b value. The statistical analysis showed that the significant factors in the extruded samples were protein content ($p = 0.0207$) and pH ($p = 0.0010$). Thus, samples extruded having low protein content and at low pH had the highest L values. On the other hand, barrel temperatures and feed moisture did not show significant effects on L values. Thus, the increasing of WPC in the blends decreased luminosity (L values) and increased b values. In general the b color parameter of the blends showed significant effects from protein content ($p < 0.0001$), and pH ($p = 0.0026$). Feed moisture did not show significant effects ($p = 0.8883$), although it showed significant effects in its interaction with pH ($p = 0.0096$). On the color scale, the b coordinate is a measure of yellowness. The b values increased when protein content and pH were increased. At low feed moisture, b values increased as pH values were increased. High levels of protein ($p = 0.0026$) and pH (0.0196) increased ΔE values. The highest ΔE values were for the blends extruded at alkaline pH. Also, Onwulata et al. (2006) reported a significant increase in b color values and a decrease in ΔE values of whey protein isolate (WPI) extruded under acidic and alkaline conditions related to raw WPI. However, the b values found in this research were higher and the ΔE values were lower, which was attributed to the high L values of CS. Similar to the findings of Onwulata et al. (2006), the high b values of extruded blends under alkaline conditions were probably due to the effect of ammonium sulfide. Substituting WPI in expanded corn meal increased lightness even at high temperature ($>140^{\circ}\text{C}$), where browning was expected (Onwulata et al. 2003). The changes in color intensity are caused by the Maillard reaction between reducing sugars (dextrinized starch) and amino groups from casein (Wen et al. 1990). However, high casein concentration, at high or low feed moisture concentration, facilitates the reaction with reducing sugars, thus intensifying the change in color when the barrel temperature is increased (Hsieh et al. 1990). The color intensity of extruded casein-starch blends is also increased by high starch concentrations due to the presence of reduced sugars because of starch dextrinization, especially at higher barrel temperatures, from 126 to 194°C (Fernandez-Gutierrez et al. 2004).

5. *In vitro* Digestibility

Statistical analysis showed that the significant effects for this response variable were protein content ($p = 0.0020$) and pH ($p = 0.0084$). High levels of these parameters results in high *in vitro* digestibility values; the effect of barrel temperature and feed moisture were not significant (Table 2). The blend extruded with 25% protein content and alkaline pH (8), had the highest value of *in vitro* digestibility. On the other hand, the samples processed with low protein and low pH had the lowest digestibility values. The extrusion process can improve

protein digestibility by its denaturation, thus increasing protein susceptibility to enzymatic hydrolysis. However, some interactions can decrease digestibility due to non-enzymatic browning reactions and the formation of cross linking reactions (Camire et al. 1990, Arêas 1992, Ledward and Tester 1994, Camire, 2000, 2001, Moraru and Kokini 2003). SDS-PAGE electrophoretic analysis of WPI and various heat-treated samples showed that even at the highest barrel temperatures the extrusion process does not affect the overall protein percentage (Onwulata et al. 2003). Furthermore, these researchers reported that although the amount of denatured protein increased with increasing temperature, denaturation had a minimal overall effect on protein digestibility. Therefore, the interesting result is the increased protein denaturation without a significant loss of digestibility due to extrusion below 100°C. The values of digestibility of extruded WPI reported by these researchers varied from 84.5 to 89.6%, slightly higher than the values found in this research. Probably due to the low barrel temperatures (<100°C), and high feed moisture (30%) used.

Table 1. Experimental design for extrusion and physical appearance of extruded blends.

Factors					Physical appearance of extruded blends
Assay	P (%)	FM (%)	pH	BT (°C)	
1	25	30	8	70	
2	25	18	3	70	
3	5	30	3	70	
4	15	23	5.5	70	
5	5	18	3	70	
6	25	30	3	70	
7	5	18	8	70	
8	25	18	8	70	
9	15	30	3	125	
10	5	18	5.5	125	
11	25	23	8	125	
12	15	18	8	180	
13	25	18	3	180	
14	5	30	8	180	
15	5	23	3	180	
16	25	30	5.5	180	

P= Protein content in the blend; FM = Feed Moisture; BT=Barrel Temperature.

Table 2. Physicochemical characterization of extruded blends of corn starch and whey protein concentrate.

Assay	Response variables								In vitro diges.
	EI	BD	WAI	WSI	Color			ΔE	
					L	a	b		
1	1.3	1000	3.45	6.84	84.35	-1.65	121.36	11.62	87.69
2	1.4	1200	4.81	24.36	85.15	-1.42	11.75	10.89	85.61
3	1.4	1000	3.76	7.82	87.81	-1.85	10.78	9.82	83.25
4	1.3	1000	3.75	11.29	87.58	-1.93	12.25	11.27	86.09
5	1.4	1100	3.71	22.85	79.66	-0.83	8.46	10.41	81.99
6	1.4	900	3.30	13.96	85.80	-0.60	11.94	11.08	85.06
7	1.5	1400	4.88	13.70	84.71	-2.16	10.80	10.01	85.39
8	1.4	1200	5.15	12.54	83.16	-1.77	15.74	15.18	85.24
9	1.3	1000	4.19	24.98	87.29	-1.07	10.65	9.70	84.88
10	1.4	1100	4.90	9.41	87.97	-2.20	10.79	9.84	84.12
11	1.3	1000	4.75	12.65	84.47	-2.00	13.11	12.32	85.84
12	0.6	1600	4.80	13.06	85.89	-1.47	12.61	11.66	85.81
13	0.7	1000	4.43	16.75	87.15	-1.29	11.28	10.30	85.06
14	0.6	1100	7.09	7.63	83.94	-1.42	10.16	9.66	Nd
15	0.5	1200	5.33	12.12	88.99	-1.86	9.46	8.73	83.14
16	0.7	1000	5.58	8.56	85.79	-1.04	12.68	11.76	86.29
CS	-	-	2.13	6.15	94.22	-2.01	4.89	8.36	Nd
WPC	-	-	6.32	79.60	79.86	-0.56	15.85	16.46	87.49

EI = Expansion Index; BD =Bulk density ($\text{Kg}\cdot\text{m}^{-3}$); WAI = Water absorption index; WSI = Water solubility index.

b. Rheology

The phase angle for the starch-protein before and after extrusion is shown in Figure 3c. Figures 3a and 3b show the frequency dependence of the storage and elastic modulus for 15% protein blends. Before extrusion, the storage modulus increased when the pH was higher, and it was the most important factor on the storage modulus. The moisture level was important too; a higher moisture level resulted in a higher modulus. An interaction between moisture and protein levels was detected, showing higher modulus when both levels were higher. In the extruded samples, pH was the most important factor, showing higher modulus for higher pH values. In this study, the frequency dependence of the moduli for all the samples was marginal. This indicated the presence of permanent junction zones forming a mechanically stable network within the experimental frequency range. The firmness of the gel depends on

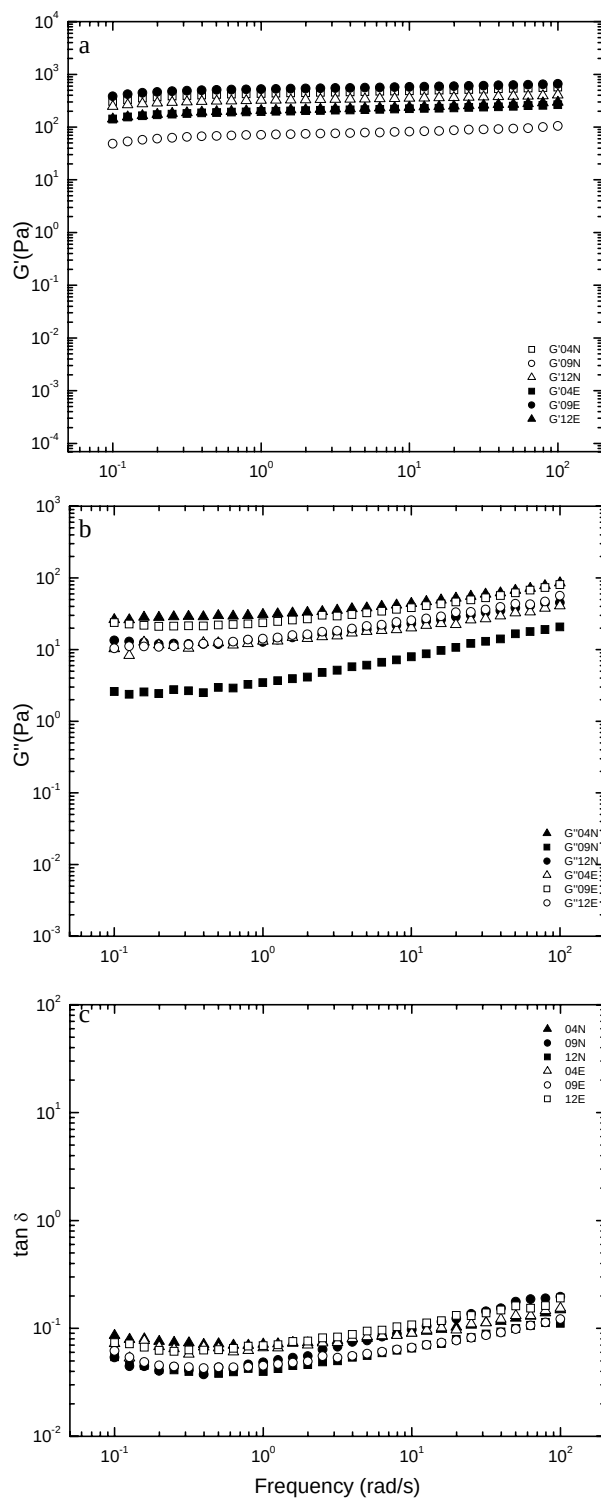


Figure 1. Variation of the storage (a) and loss (b) moduli and loss angle with frequency from 0.1 to 100 rad/s at 25 °C, for CS-WPC80 blends (85-15) before (N) and after (E) extrusion .

the extent to which junction zone are formed. There is evidence that most protein and polysaccharide systems form phase-separated solutions (Braudo et al. 1986). Phase separation can be accompanied by water partitioning between phases. This can lead to an increase in the concentration of the biopolymers in one of the phases and a correspondent dilution in the other phase (Tolstoguzov 1995). Muhrbeck and Eliasson (1991) studied the gelation rates at 90 °C of pure bovine serum albumin (BSA), potato starch, annealed potato starch and cassava starch (CaS) systems as well as 1:1 protein/starch mixtures of the same components using oscillatory tests, at a frequency of 1.0 Hz and a strain of approximately 0.04. The gap between the parallel plates was 0.5 mm. They found that both the transition temperature and the rates of gelation of the components were critical for studying the behavior of complex systems. They also measured values of the G' of CaS starch/BSA gels as a function of protein fraction at 10% total solids (TS), heated to 90 °C and cooled to 25 °C. They reported that gels with a starch fraction greater than 0.6 showed low G' (less than 0.1 kPa), and when the starch fraction decreased, the modulus increased dramatically at least by five times. The starch fraction range considered was between 0 and 0.25. The measurements were performed in oscillatory mode at a frequency of 1 Hz and strain values near 0.02. Aguilera and Rojas (1996) studied mixed gels of CaS and WPI obtained by heating of 10% TS, at pH 5.75 to 85 °C, that were characterized as a function of the starch fractions by small amplitude oscillatory rheometry and DSC, and reported that in the range of starch fraction between 0 and 0.4, mixed gels showed higher storage modulus properties than individual gels. Viscoelastic measurements as a function of time showed that gels containing higher levels of WPI developed larger G' . G' and G'' were determined at a frequency of 1.0 Hz under a maximum deformation of 0.5% (within the linear viscoelastic region) to ensure preservation of the gel structure. Data showed a rapid initial increase in moduli, representative of the sol-gel transition. There are food products in which the gel network consists of polymer chains. The ability of the chains to interchange at any point in the network and the lifetime of the cross-links depend on the nature of the cross-link points or “junction zones” (Biliaderis 1992). Polymer molecules are joined in junction zones by hydrogen bonding, hydrophobic associations, and ionic and covalent bonding. On the other hand, Pateras and Rosenthal (1992) suggested, that the starch granules may well gelatinize after being immobilized in the protein network, disrupting the protein matrix upon further swelling, therefore weakening the structure of gel.

c. Surface Hydrophobicity

Fluorescence intensity of protein solution increased as ANS molecules bound to specific binding sites on protein molecules. The statistical analysis showed that the extrusion process had effect in S_0 ($p = 0.0043$). Denaturation and aggregation of WPC in the presence of added corn starch at pH 3 resulted in an increased S_0 . This increase is due to protein denaturation which may lead to the unfolding of protein molecule and thus exposing hydrophobic regions. Similarly, Mleko et al. (1991) reported that denaturation and aggregation of WPI protein by addition of κ -carrageenan at low pH caused an increase in surface hydrophobicity. These changes at highly acidic pH's were attributed to non covalent monomer-dimer transitions of β -LG by Das and Kinsella (1989). However, lower surface hydrophobicity values observed in extruded samples are probably due to the interactions between starch and whey proteins.

Thus, ANS fluorescence reflects the changes occurring around these binding sites, and can be used to detect structural and functional modification in the protein molecules.

d. Degree of Denaturation

The effect of extrusion parameters and temperature was evaluated through observation of whey protein denaturation measured by reverse phase high performance liquid chromatography (RP-HPLC). It could be observed that extrusion resulted in protein denaturation, however, there were other factors affecting it. Theoretically, more hydrophobic sites should be exposed when the protein is denatured. However, this effect may not be apparent when proteins aggregate together and block newly exposed non-polar sites (Bonomi et al. 1988). In this study the S_0 did not increase when protein denaturation was higher, suggesting a possible interaction between starch and denatured whey protein.

Table 3. Surface Hydrophobicity (S_0) of extruded blends and denaturation degree (%) of protein.

Assay	Surface Hydrophobicity, S_0		Denaturation degree (%)	
	20 mM Tris-HCl buffer, pH 6.7		Protein Total	
	Before extrusion	After extrusion	Before extrusion	After extrusion
1	186.35	79.86	28.6	65.3
2	552.61	64.35	26.9	93.4
3	112.35	48.61	95.0	97.6
4	268.16	46.43	26.7	82.4
5	393.94	68.29	93.9	99.6
6	516.83	186.59	33.5	69.6
7	333.00	52.03	90.2	100.0
8	262.24	11.94	4.8	100.0
9	442.99	12.91	39.8	99.9
10	273.94	33.19	92.2	99.6
11	228.81	32.15	17.3	69.1
12	281.24	16.85	14.9	100.0
13	504.22	6.86	17.5	100.0
14	153.49	18.55	94.4	100.0
15	247.56	44.10	92.8	99.6
16	245.22	15.99	28.3	100.0

Related to protein content (3.1 mg/mL)

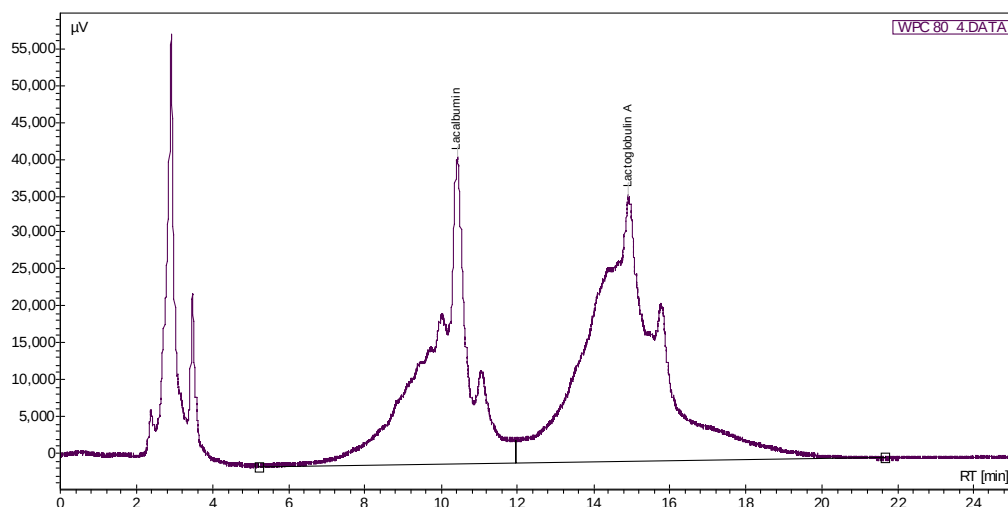


Figure 2. Typical chromatogram of WPC 80.

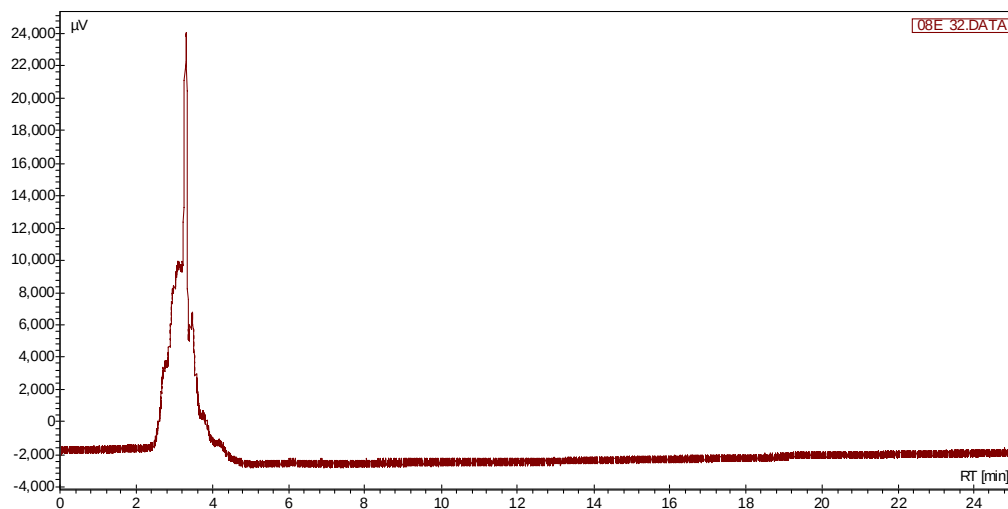


Figure 3. Chromatogram of CS-WPC (75-25%), 18% moisture, pH8 after extrusion at 70 °C (assay 8).

e. Application of Extruded-Milled Corn Starch-Whey Protein Concentrate Blends in Foods

1. Cheese Analogue

The multivariable profile of global performance of the extrusion treatments showed an association between medium and high levels of moisture content of the raw material with the maximum values for the response variables, mainly for viscosity and gel force. These two parameters are important for achieving good incorporation of the ingredients when making the cheese analogue. In accordance with the response variables, 9 assays of the extruded blends were selected to prepare the cheese analogue. The data obtained (Figure 4) from melting, texture elasticity (ELS), cohesiveness (COH), chewiness (CHE), gumminess

(GUM), adhesiveness (ADH), hardness and yield tests of the cheese analogues were compared to Oaxaca-type commercial cheeses (Table 4). The results obtained showed a good level for texture and appearance attributes. The versatility of extrusion technology offers the possibility of obtaining SM-WP blends with acceptable functional properties which provide alternatives for partial substitution of casein in making Oaxaca-type cheese analogues.



Figure 4. Cheese analogue manufactured using functional extruded-milled corn starch-whey protein concentrate blends. Final appearance of the cheese.

Table 4. Melting and Texture Profile Analysis (TPA) for cheese analogues elaborated and two commercial cheeses.

Assay	M	ELS	COH	CHE	GUM	ADH	H
1	5.15	0.622	0.457	1.461	2.371	-0.038	49.064
3	2.75	0.58	0.409	1.374	2.416	-0.062	51.009
4	3	0.522	0.403	1.02	1.955	-0.026	47.579
6	1.9	0.514	0.32	0.902	1.792	-0.057	52.729
9	2.7	0.469	0.349	1.027	2.169	-0.06	60.5
11	4.55	0.565	0.456	1.509	2.665	-0.054	56.899
14	3.2	0.627	0.338	0.986	1.591	-0.014	41.055
15	3.2	0.454	0.3	0.441	0.971	-0.008	31.772
16	3.55	0.459	0.341	1.09	2.378	-0.045	68.277
C1	6.6	0.702	0.631	1.399	1.998	-0.037	31.176
C2	2.2	0.744	0.472	1.2	1.95	-0.006	40.195

M = Melting (cm), ELS = texture elasticity, COH = cohesiveness, CHE = chewiness, GUM = gumminess, ADH = adhesiveness, H = Hardness (N), C1= Commercial Oaxaca-Type cheese, 100% milk, C2= Cheese analogue Oaxaca-Type Commercial 2.

2. Yoghurt-Like Drink

Yoghurt-like drink added with 50, and 75% of the extruded blends (assays 7, and 8) (Figures 5a, and 5b) showed a decrease in pH similar to the control (traditional drinking yoghurt) during the two first hours of fermentation. Similar tendencies to the previous assays were found in the development of acidity, although, with lower values in relation to the control sample. Only the control yoghurt (2.4%) and the yoghurt added with the assay 8 at 75% (6.1%) showed syneresis. Assay 7 showed similar yoghurt viscosity to the control (Figure 6). Yoghurt added with the assay 8 at 50 and at 75%, in the preparation of drinking yoghurt had the best scores in sensorial properties.

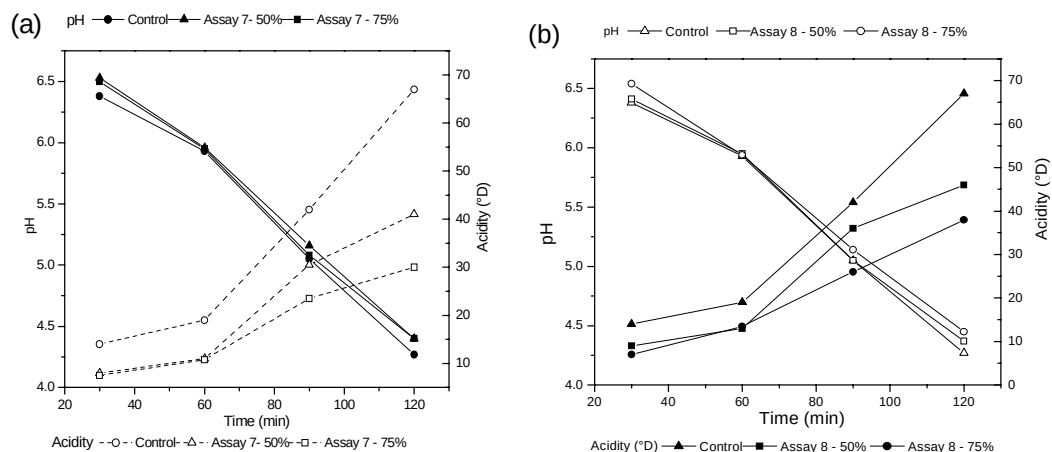


Figure 5. Development of pH and Acidity (°D) in yoghurt during the two first hours of fermentation.

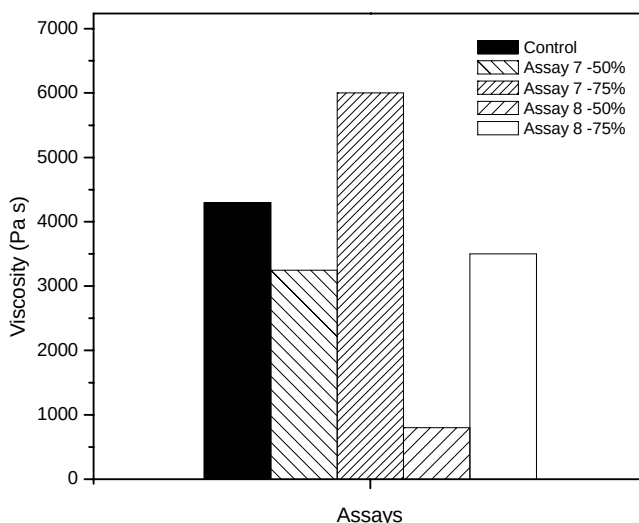


Figure 6. Viscosity of yoghurt-like drink and control yoghurt. The percentage shows the milk substitution level in the formulation.

V. Conclusions

The global effect of the four factors analyzed during extrusion influenced the structural and functional properties of the extruded blends. High barrel temperatures and protein concentration decreased the expansion index of the blends. Blends extruded with high protein concentration and pH increased the yellow color of the blends. The water absorption index and water solubility index varied according to the processing conditions, although the effects of the acidic conditions during extrusion were more important among response variables. Protein concentration and pH were the most important variables influencing the digestibility *in vitro*, although in general, most of the blends improved their values. Surface hydrophobicity is a good indicator of hydrophobic sides availability for interaction in food systems. S_0 was used in this study to probe interaction between corn starch and WPC during extrusion process. Results showed that S_0 are affected by processing parameters of extrusion and it can be used to monitor the interaction between proteins and carbohydrates. Our findings revealed the importance of pH in combination with extrusion conditions in the manufacture of diverse extruded blends of starch and WPC. Newly produced texturized blends could be utilized in new food product formulations such as Oaxaca-type cheese analogues and yoghurt-like drink.

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Chapter 8

ON-LINE QUALITY ESTIMATION FOR THE COFFEE BATCH ROASTING

J.A. Hernández^{a,}, B. Heyd^b, G. Trystram^b and C. Irles^c*

^a Research Center of Engineering and Applied Sciences (CIICAp),
Autonomous University of Morelos State (UAEM); Av. Universidad
No. 1001 Col. Chamilpa, C.P. 62209, Cuernavaca, Morelos, México

^b Joint Research Unit Food Process Engineering
(Cemagref, ENSIA, INAPG, INRA) ENSIA, 1 avenue des Olympiades,
91744 Massy Cedex France

^c National Institute of Perinatology, Montes Urales 800,
Lomas de Virreyes, CP 1100, Mexico, DF

Abstract

In order to guarantee and optimize the quality of a good cup of coffee, roasting is a key step in the process. In this roasting step the green beans are heated at high temperatures (over 190 °C), initiating a series of complex chemical reactions, which lead to the formation of essential substances to give among other, the sensory quality of the cup of coffee. Consequently, roasting is essential to control a large number of factors. Today's, robust sensors and algorithms are used to measure and on-line analyze essential factors such as color, surface, temperature, weight,... In this work, a control strategy is applied to on-line estimate the quality of roasted coffee. Coffee beans were roasted using hot air as heating medium. Bean temperature, weight, color and surface were measured on-line during roasting. These experiences allow better understanding of the phenomena that appear during roasting. A dynamical model was used to describe the heat and mass transfer of the beans while the gray values and expansion kinetics of the beans were estimated by an artificial neural network. The neural network considers the simulated temperature of bean and roasting time during the process. This strategy allowed us to estimate the quality of roasted coffee, when the roasting degree wished is similar to the gray value obtained by the model. These results were in good agreement since the roasted coffee was evaluated experimentally. Therefore, it is possible to apply this strategy in the industry to guarantee the quality of coffee roasting.

*E-mail address: alfredo@uaem.mx. Tel: 52(777)3297084. Fax:52(777)3297984. (Corresponding author)

1. Introduction

In order to obtain a good cup of coffee, the step of roasting is very important to develop specific organoleptic properties (flavors, aromas and color), underlying the quality of the coffee. The amount of heat transferred to the bean is essential in the roasting process. The process can be divided into two phases. The first phase corresponds to the drying (bean's temperature below 160 °C) and the second phase is the roasting (bean's temperature between 160 and 260 °C). In this last phase, pyrolytic reactions start at 190 °C causing oxidation, reduction, hydrolysis, polymerisation, decarboxilation and many other chemical changes, leading to the formation of substances essential to give among other, the sensory qualities of the coffee. These moisture loss and chemical reactions are accompanied by important changes (color, volume, mass, form, bean pop, pH, density, volatile components) and generate CO_2 , of which a part escapes and other part is retained in the cells of the beans. After this second phase, the beans must be rapidly cooled to stop the reactions (using water or air as cooling agent) and to prevent an excessive roast which alter the quality of the product [1, 2, 3, 4].

During the process, several parameters can be used as indicators to determine the degree of roasting (aroma, flavor, color, bean's temperature, pH, chemical composition, bean pop, mass loss, gas composition and volume) [5, 1, 11, 12, 2]. Nevertheless, in the industry, in order to obtain the optimal degree of roasting and to control the quality of the product, the roast master take up an essential position. In one hand, he interprets the physic measure (temperature and time of stay), and in the other hand, the organoleptic properties of the coffee beverage (color, aroma and flavor). However, these measures are obtained out-line.

The principal target of image anlysis is to help the human pecerption of the visual phenomena (progress of the images or reconstruct of the image) from the optical creation of systems of measurement using the color and the magnitude, and in addition for provide controls of the environment for the systems robotics [6]. The evaluation on the quality of the produits in the food industries is in most cases constituted by the sensory, microbiological and nutritional aspects. The sensory aspects as color and arome are important for the frist appreciation of a coffee roasted, because the taste and the texture are not facil to on-line evaluate by the roasted master. Therefore, the color is a parameter to control. Today, the sensors and algorithms of image analysis allow to analyse the properties of final product and during the process, using essencial values such as the color, the surface and visual texture [6, 5, 7].

Automation is limited by the lack of captors allowing to follow the quality in real time, and by the process conditions (the mass of beans is always in agitation) which make instrumentation difficult [1, 5]. It is important to mention that the control of temperatures and duration, in industry, are only effective, if the quality of the raw material does not vary. Today, the chemical reactions are extensively studied by Illy and Viani[2], nevertheless, coffee roasting is slightly studied as an unit operation. Indeed, in this operation, a specific instrumentation, working in real time and taking into account the variables of the product does not exist. Several variations are presented as a function of the raw material and of the process conditions.

We identified the need of building a trustworthy experiemntal implement and respectable as well as also the construction of models. Therefore, the aim of this work is

developed an experimental system capable of providing on-line the color, surface, temperature and mass of the bean during the coffee roasting and to evaluate the quality in the purpose of process control. For the color and surface kinetics, the architecture of this implement is constituted by an image analysis system (video camera CCD, 2 spots and source of light), a roaster working with air heat, and different algorithms developed in the language *C*, *bash* and *octave* of Linux.

2. Material and Methods

2.1. Green Coffee

Colombia green coffee beans (*Arabica*) are roasted using hot air flow as heating medium. The experiments are carried out at constant air velocity of $4 \frac{m}{s}$ for constant air temperatures (190, 200, 210, 220, 230, 240, 250, 260, 270, 280, 290 and 300 °C) during 10 minutes. The experiments are done with three replicates.

2.2. Temperature and Mass Acquisition System

Figure 1 depicts the data acquisition and processing using a computer equipped with a temperature acquisition system (SCB7 thermocouple conditioner and Arcom PCAD12/16H A/D converter) and several software. The low level task (data acquisition and I/O port programming) are written in *C*, real time data processing are done with *Octave* [13] and algorithm is managed in *bash* [14]; Type *K* Thermocouples allowed to measure internal and external temperatures of the beans and to control the air temperature with a precision of ± 0.5 °C. One bean is drilled in order to insert a thermocouple 4 mm below the surface (internal temperature), and another thermocouple about 0.2 mm below the surface in order to measure the near surface temperature (see Fig. 1B). The beans are placed on a mesh to keep them on static suspension, where convection is the predominant mode of heat transfer. Beans weight is automatically measured using an electronic scale METTLER (SB16001) and controlled by the computer (see Fig. 1A). A program written in *bash* makes the weight acquisition each minute. Before each weight acquisition, the fan of the roaster is automatically stopped for 8 s to stabilize the measure.

2.3. Image Acquisition System

A static roaster (SERVATHIN Series SV02 7817) was used to carry out the roasting experiments. A schematic draw of the roaster is given in Fig. 2. The coffee beans were placed on a mesh to keep them on static suspension, where convection is the predominant mode of heat transfer. This coffee roaster allowed us to equip it to achieve the aim raised. During coffee roasting the obtained direct measures were the air temperature in the roaster from a temperature acquisition system and the coffee beans images by an image analysis system.

Figure 2 shows the experimental system developed to follow the on-line color [Red, Green and Blue] or the level of bright intensity (gray level) and the on-line surface of the coffee beans during roasting. This experimental system is constituted as all the device classic of image analysis:

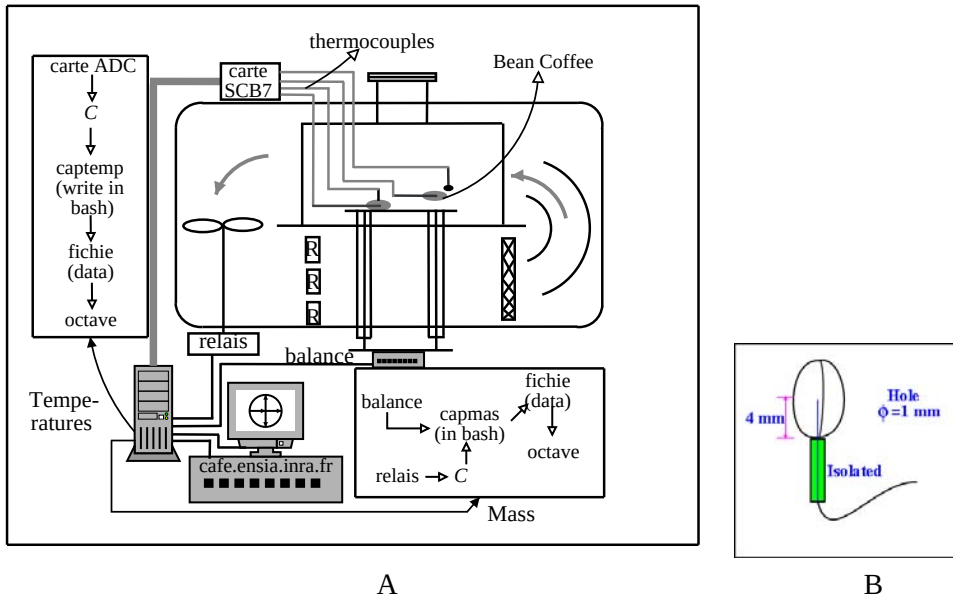


Figure 1. Scheme of experimental data used (temperatures and mass).

- A system of illumination: a source of light with two small spotlight of fibre optics are establish for the illumination of the scene,
- A sensor of image: a camera video CCD (Charge-Coupled Device) color RGB (red, green and blue) SONY (XC-711P) working with an objective 50 mm ϕ 25.5. This type of sensor is an of the less expense,
- A system of numeration: a computer is used, which is provided with one card of acquisition video *Hauppauge WinTV* equipped with a converter *bttv 878*, allowing the numeration of the image. We deliberately applied these equipments general public for their robustness to lesser expense, but especially the availability of the source codes of the software pilots of the component *bttv 878*.

and to the air temperature acquisition is given by the following:

- Thermocouples (type K) to measure the air temperature with a precision of ± 0.5 °C,
- An Arcom SCB7 thermocouple conditioner connected to the personal computer and,
- An Arcom PCAD12/16H A/D converter for the acquisition of air temperature in the roaster.

The data acquisition and I/O port programming are written in C [8, 9], on-line data processing is done with a program written in *Octave* [13] and an algorithm is managed in *bash* [14].

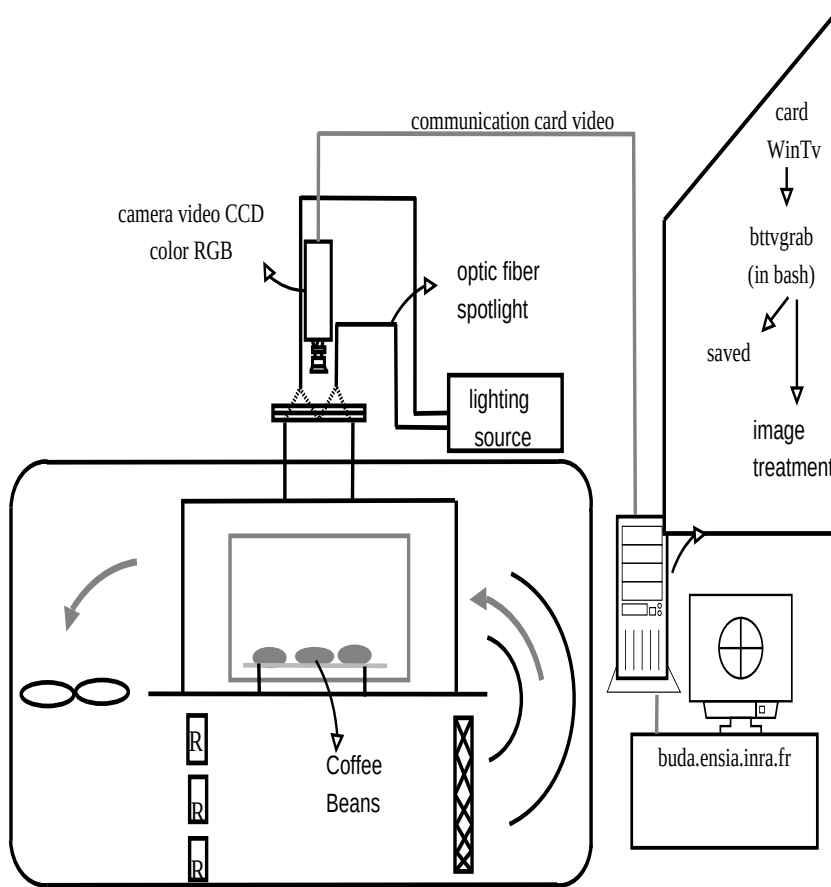


Figure 2. Acquisition scheme of experimental data used (color and surface).

2.4. Image Processing System

As shown in Figure 2, the camera video is installed outside the room of roaster and visualises the scene through a glassy window which introduces a distortion neglected by the optic way. The images acquisition are made by using the software *btvgrab* (command *btvgrab -s1 -Q -l1 -oppm -dq -w640 -W480*) [10]. This software has the advantage to be used in a program written in *bash*. The images are saved onto the hard disk in format *ppm* (portable pixel map) at regular intervals of time (an image every twenty seconds) with a definition of $480 \cdot 640$ pixels in R,G,B, and gray values. The images visualisation is carried out with the software *xv*. Therefore, the image system is constituted by three stage: the acquisition (visualisation of the objects, numeration), the treatment and the extraction of information. It is important to notice that all these measures (air temperature, color (RGB and gray level) and surface) are acquired on-line allowing this way to take decisions of the process in real-time.

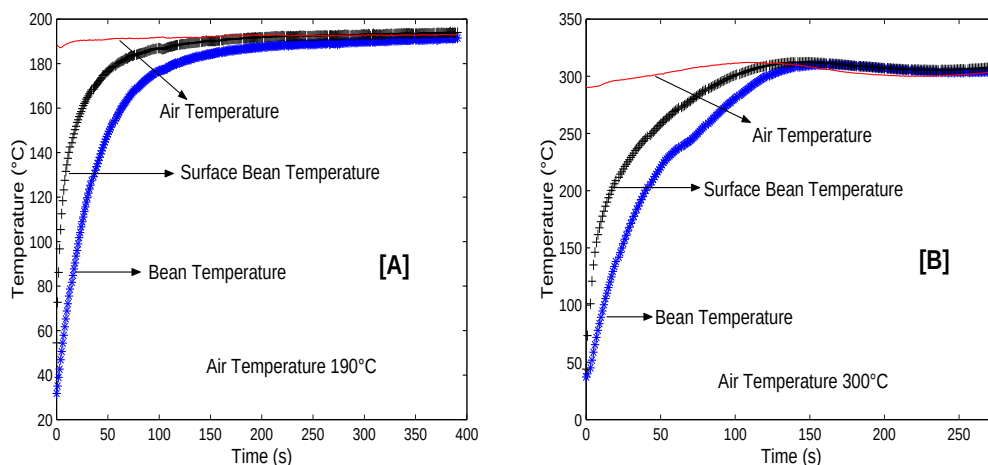


Figure 3. Evolution of bean's temperatures for roasting at 190 °C and 300 °C

3. Results and Discussion

3.1. Temperature and Mass Experimental Data

During coffee roasting, mass and temperature are measured on-line. The results will allow a better understanding of the process, and a validation of the mathematical model.

Figure 3 shows the evolution of the internal and external bean's temperature and of the air temperature (in °C) during the roasting. These curves (Fig. 3) put in evidence the effect of the air temperature on the evolution of the bean's temperature. The internal bean's temperature has an exponential behavior described by Schwartzberg [1] if bean's temperature is below 250 °C.

An evident deviation with exponential kinetic is observed between 80 and 100 seconds of roasting (Fig. 3b) for experiments where the bean's temperature become higher than 260 °C. When the optimal bean's temperature is surpassed, the exothermic reactions responsible of the aroma and flavor are reduced and the beans begin to be burn. This phenomenon is called over-roasting by Coste [15], it can be responsible of the observed deviation. Consequently, this confirm that the bean's temperature versus the time can be an indicator of the roast-degree during coffee roasting. It is important to mention that Schwartzberg [1] stopped the process when the bean temperature reach 238 °C, so he never observed this phenomenon.

During roasting, weight loss is measured each minute. The results in Figure 4, show that we obtained a good repeatability of the measures (two repetition at 300 °C and 190 °C, and three at 250 °C). After a short stage of latency, we observe a quasi linear behavior followed by a marked deceleration. Weight loss clearly depend on the air temperature of the roasting time. After 10 minutes of process the percentage of mass loss ranged from 3% to 12% depending on roasting temperature. Similar results are reported by several authors [16, 12, 1, 17]. This authors also reported weight loss differences due to types of roasting machines, duration, type of bean and air temperature.

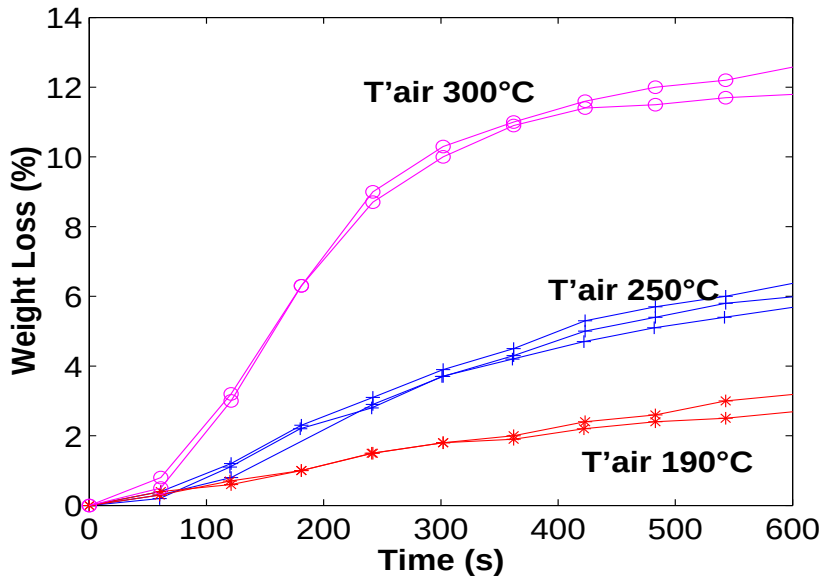


Figure 4. Experimental kinetics of weight loss

According to Illy and Viani [2, 18], the moisture content is about 8-12% d. b. in green coffee and below 5% d. b. in roasted coffee. Furthermore, volatile components are formed during roasting, inducing also noticeable mass loss. Dutra et al., [12] determined weight loss during the process for 300 g of green coffee using a direct heating. They found two different speeds for mass loss: the first period, between 0 and 7 min, shows a linear kinetic with a weak slope, this period corresponds to a moisture and volatiles losses, the second period from 7 to 12 min the weight loss follows a right line with a strong slope, and this corresponds to a loss of CO_2 and organic components of the bean. Besides, they showed that loss of CO_2 increases when the moisture content diminishes significantly. The evolution of the mass loss can therefore be a criterion of the roasting degree, but it is not a key criterion for us because weight is difficult to measure on-line in the industry.

3.2. On-Line Color (Gray) from Images during Coffee Roasting

The main of the image treatment and extration is to have means to on-line control the roasting process considering parameters (color and swell), to determine the degree of coffee roasting. In spite of the precautions which we brought on the measure, the images are taking in the conditions similar to the industrial way. However, it is difficil of control absolutely the illumination. Therefore, the images depend of the experimental conditions, because there is a heterogeneity in the scene (every point of the image not recive neither the same quantity nor the same quality of lighting). Consecuntly, in each image obtained is considered their heterogeneity of the scene [5]. As results, the information is obtained by 3 matrices (R,G,B). In order to working with this information ($3 \cdot 640 \cdot 480$) and to reduce the time of calculation in computer, the equation 1 is considered for obtaine 1 matrnx of $640 \cdot 480$:

$$\text{gray level} = \frac{\text{Red} + \text{Green} + \text{Blu}}{3} \quad (1)$$

It is possible to make an experience in real-time with the proposed image acquisition system, to stop the process when the coffee roasting grade is optimum. For the previous thing, the [R, G, B] beans values are known in every acquisition by the camera video CCD and the treatment and information extraction of the image by the written program in Octave. Therefore, the gray level of every image can be on-line compared with the gray level optimum value of a coffee already roasted. In this case, the coffee already roasted is used by three different types of coffee roasted in the industries (three different roaster master). These R, G, B, optimum values are obtained in the proposed images acquisition system and that correspond at the coffee already roasted by the 3 companies: a) coffee roasted (*Arabica*) has as values of [Red=56.4, Green=75.0 and Blu=80.1] and therefore the gray level is equal to 70.5; b) coffee roasted (*Arabica*) has as values of [Red=55.3, Green=72.9 and Blu=77.5] with gray level of 68.6 and finally, c) coffee roasted (*Robusta*) has values of [54.8, 71.7, 78.3] with gray level of 68.3. It is very interesting to notice that the difference between the values of R, G, B, for the three companies are minimal. This is very important, because the color of coffee beans are almost the same. The small difference can be due to the different grade of toasted and of the type of beans used (*Arabica* and *Robusta*).

The Figure 5 shows the on-line obtained gray level versus the time and with air temperature fixed by the roaster of 230 °C during the roasting. The process is considered finished when the gray level of the coffee beans attained the optimum determined by the companies (a). In addition, the figure 5 presents five images, the three first corresponds at the optimum of every companies and two last ones corresponds at the coffee green and coffee roasted beans (respectively). Therefore, it is possible to obtain a color acceptable. The obtained optimum coffee was tasted by the members of the laboratory and was considered acceptable. This test confirms that it is possible to roast the green coffee beans in the proposed system and of on-line optimizer the process.

Figure 6 represented the evolution of the level of grey of the bean of coffee during roasting with different air temperatures. In high air temperatures (≥ 260 °C) the change of the level of grey is quicker during process. The curves of grey show therefore that the air temperature and time are two important factors for the process of roasting. The repetition of the tries, noted on the curves of grey, shows a character of allowable repetition well.

3.3. Pixel Size Determination

Distance on pictures is counted in number of pixels. They depend therefore on experimental conditions and particularly on the focal length of objective and distance of objects in the camera. It is therefore necessary to play a calibration to convert distance expressed in number of pixels, in millimetres. For this calibration, we took a picture representing a circle of diameter 30 mm on a white bottom (fig. 7). They determine easily the *length* and the *height* of the circle by commanding lines or columns of the matrix of any element colorimetric of picture [R, V, B] or levels of grey, as shows it the figure 8. It can also determine the surface of the limited square in the circle in number of pixels, to calibrate the surface of this square. For it, we measured a length of 274 pixels and a height of 262

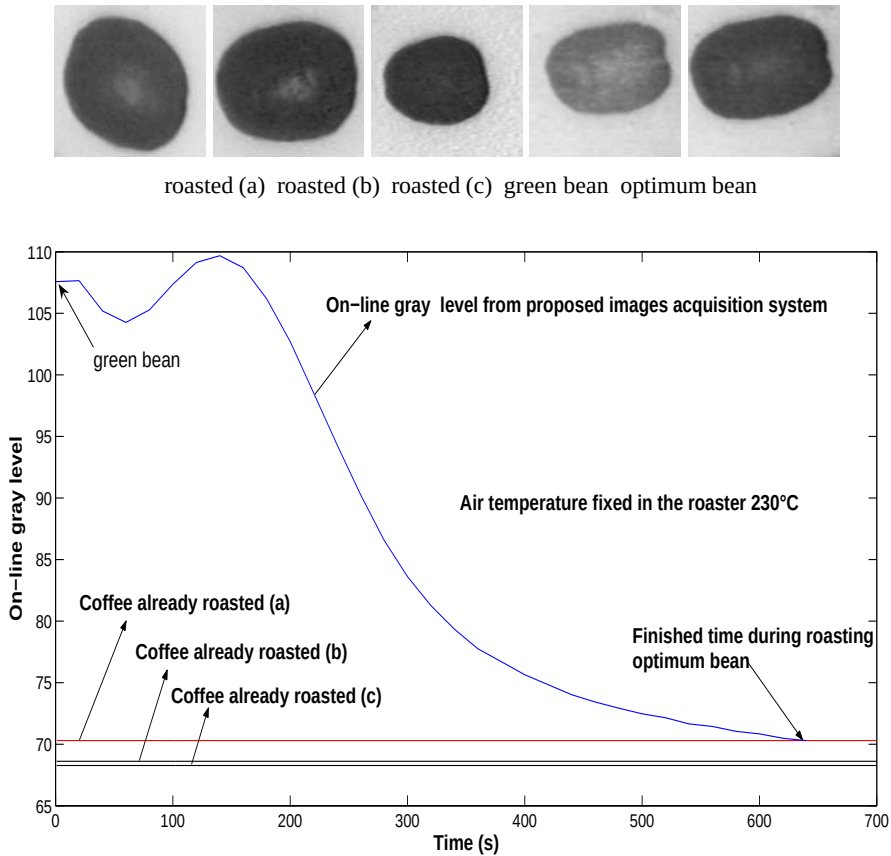


Figure 5. On-line gray level kinetic from image analysis. In addition, optimum roasted coffee is determined from different coffee beans already roasted by the industry (a, b and c)

pixels for the picture of the circle. Therefore, the square circumscribes of 900 mm^2 count therefore 71788 pixels, they deduct the surface of a pixel in our system of 0.012537 mm^2 . The surface of the pixel is stocked in a text file which will be later read in the course of the treatment of pictures. Acquired results are similar whatever is the position of the circle on picture. It is necessary to note that the length and the height should be equal, however it is not case. In effect, this baby distorsion can be owed to the space resolution of the sensor CCD which takes a sample more in width than in height.

3.3.1. Bean Surface Experimental Kinetics

After the calibration of the surface of the pixel, the surface of the grain is measured in mm^2 from the number of pixels counted on picture. The figure 9 shows the increase of the surface of beans according to the air temperature and time of roasting studied. These surface curves (fig. 9a) introduce an increase of 15% at 70% with an increase of air temperatures between 190°C and 300°C . Moreover, Schwartzberg [1] showed an expansion of volume of the bean of 50 % at 120 % for air temperatures of 270°C at 550°C with different roasted used. Dutra et al., [12] determined an increase of volume of 120 % in time of roasting of 12

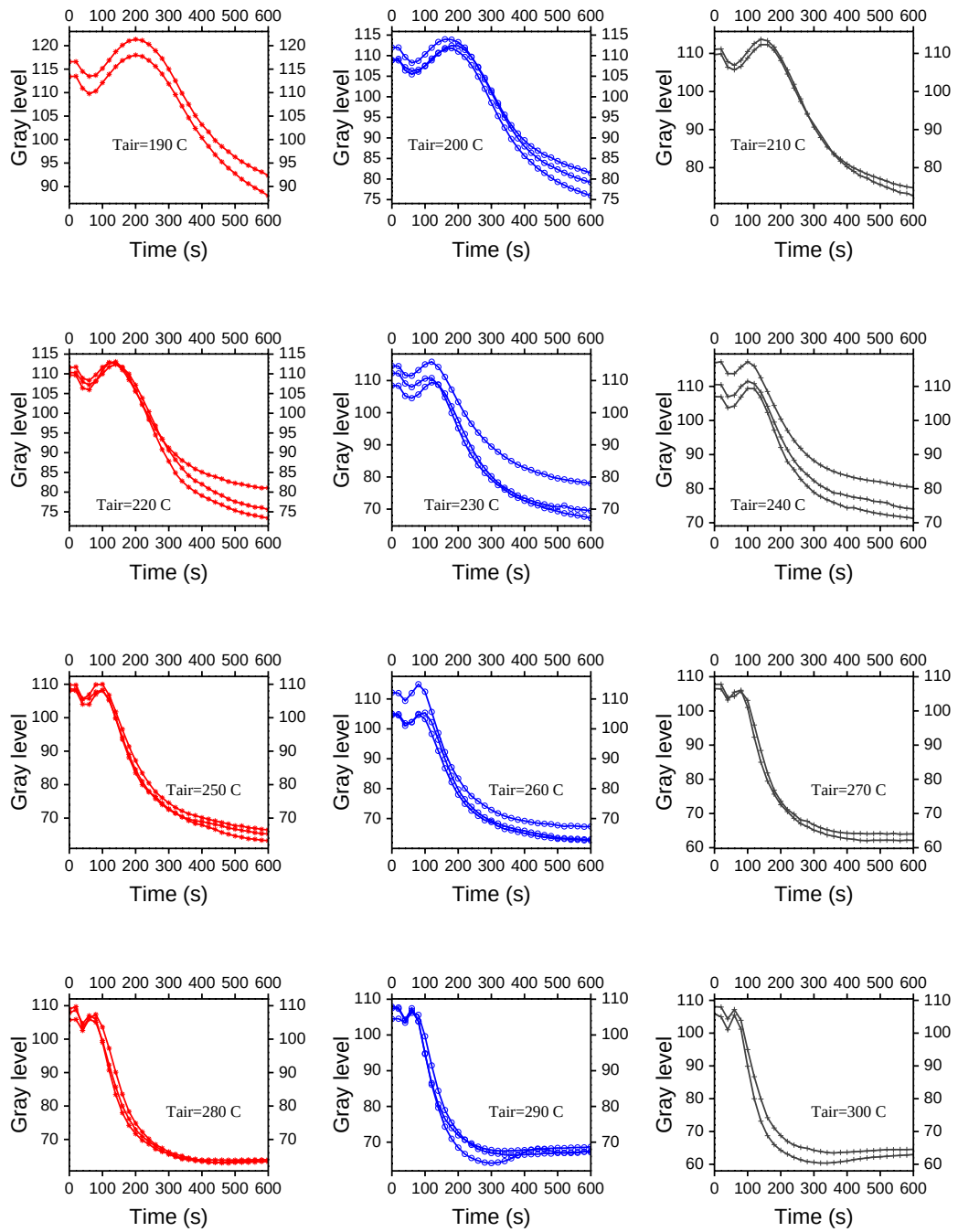


Figure 6. Gray level kinetics for all experiments and their repetitions

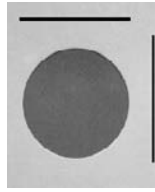


Figure 7. Diameter of the circle 3 cm

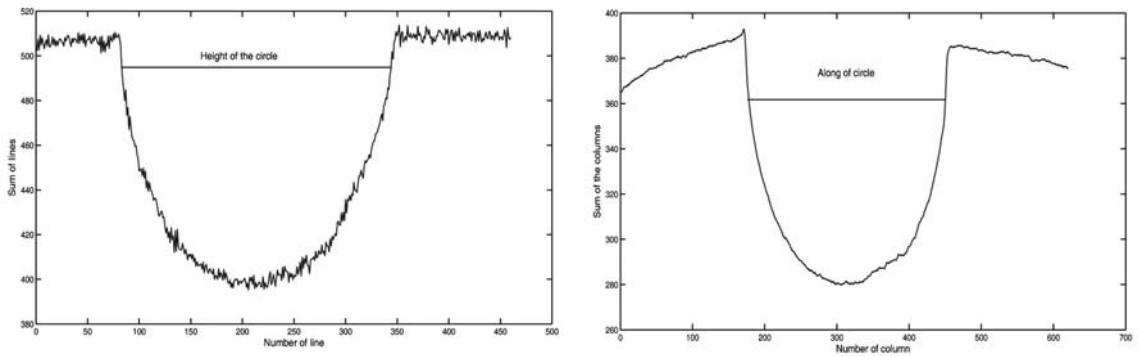


Figure 8. Analysis of the circle of calibration

min at an air temperature of 275 °C, by using a direct heating (gone about things the most ancient which is not any more used industrially). The air temperature is therefore one of the parameters key for the swelling of coffee in the course of roasting. It can also note that for air temperatures between 280°Cat 300°Cand for the upper time in 360 seconds, increase is almost ended (voir fig. 9a), this can be owed to the optimum temperature of the bean which is exceeded and consequently the roasting is finished. Coste [15] mentioned that the volume of the bean does not augment any more when temperature of the bean exceeds 280 °C.

For a better understanding of this phenomenon of increase, the figure also shows a surface kinetic and temperature of the bean according to time (Fig. 9b and Fig. 9c), for an air temperature of 190 °C. This figure 9b allows to put in an obvious place that the coffee bean begins to swell only when the internal temperature of the bean becomes the upper at 100 °C, what confirms hypothesis of Guyot [18] which allocates this expansion in pressure of water steam. On the other hand, Dutra et al., [12] mentioned that the increase of the surface is caused by 3 phenomena which take place during process of roasting: the vaporizing of water, the release of carbon dioxide CO_2 , and the estrangement of components (organic) fowls of beans, but the formation of CO_2 assume a big permeability at the O_2 walls what seems difficult if they consider that the increase of volume is owed in big one internal pressure.

It is important to mention that we made a try to analyse if the swelling of the bean is homogeneous, that is to say if the relating expansion of the bean is the same in all directions. For it, we analysed the swelling of the bean of coffee in the three different views in the

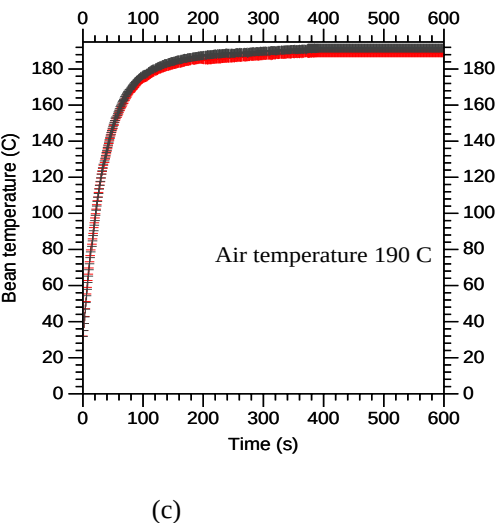
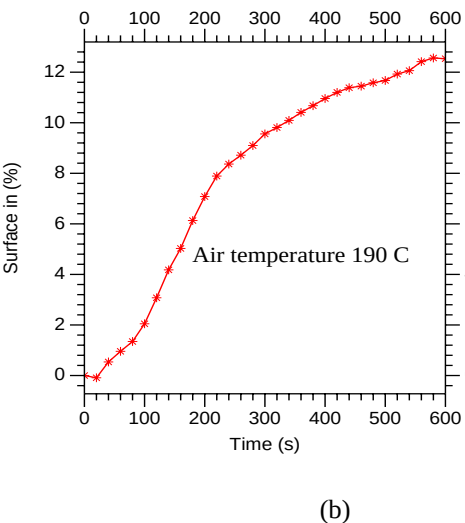
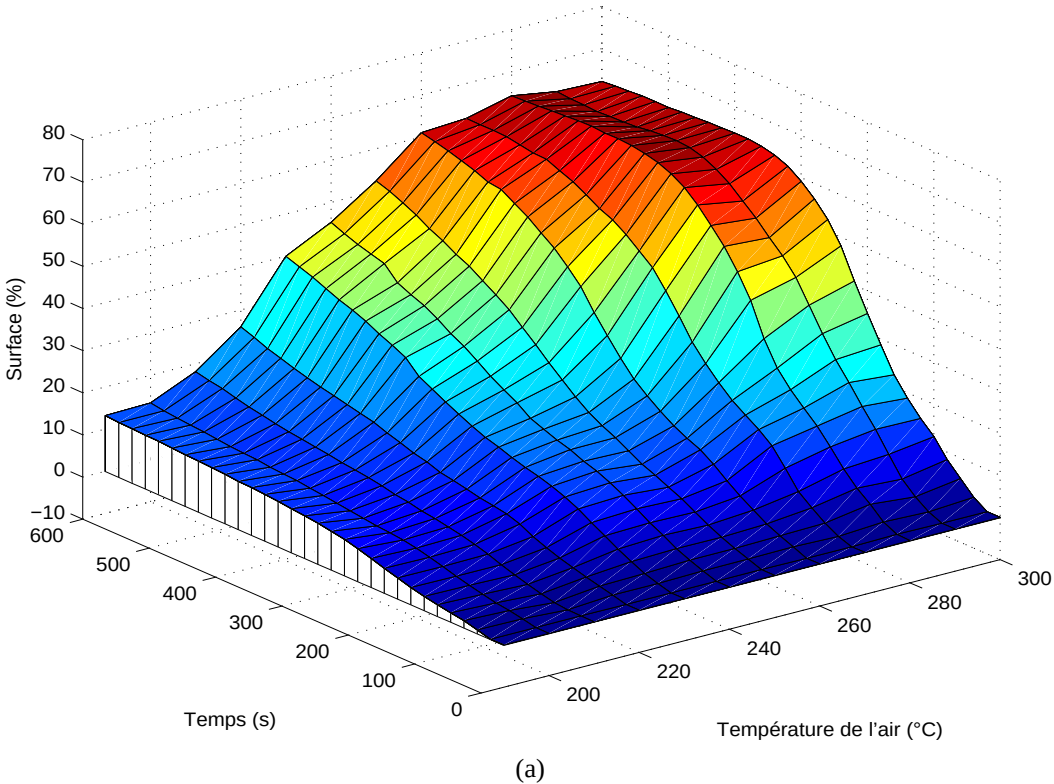


Figure 9. Experimental kinetics of increase of the surface and the bean temperature.(a) surface curves function of the time and air temperatures. (b) an experience of surface function of time. (c) the same experience but the bean temperature function of time.



Figure 10. The expansion of the bean is homogeneous, a (below), b (vertical) and c (above).

course of roasting: beans with three views of the bean (above, vertical and below, see fig. 10). We noticed that the three analysed views of beans introduced one homogeneous swelling [20]. As a result, they can easily calculate the volume.

3.4. Heat and Mass Transfer Modelling

The heat and mass transport mechanisms during batch roasting (roaster using hot air flow) are given by the equations proposed by Schwartzberg [1].

- *moisture loss*, the diffusive water transport in the bean is given by

$$-\frac{dX}{dt} = \frac{4.32 \times 10^9 \cdot X^2}{d_p^2} \exp \left[-\frac{9889}{T_b + 273.15} \right] \quad (2)$$

X : moisture content $\left(\frac{\text{kg water}}{\text{kg dry matter}} \right)$; T_b : internal temperature of the bean ($^{\circ}\text{C}$). The water loss is governed by an *Arrhenius* type equation, proportional to X^2 ; and d_p : effective bean diameter,

- *heat transfer*, the rate of temperature rise of the beans is given by

$$\frac{dT_b}{dt} = \frac{G C p_a [T_{ae} - T_{as}] - Q_{a \rightarrow m} + Q_{m \rightarrow b} + m_{bs} (Q_r + L v \frac{dX}{dt})}{m_{bs} (1 + X) C p_b} \quad (3)$$

where T_{ae} and T_{as} are respectively the in-air and out-air temperature ($^{\circ}\text{C}$). G is the air mass-flow rate $\left(\frac{\text{kg}}{\text{s}} \right)$. $C p_a$ and $C p_b$ are respectively the air and bean heat capacity $\left(\frac{\text{kJ}}{\text{kg} \cdot ^{\circ}\text{C}} \right)$. m_{bs} is the dry weight of the bean *kg dry coffee* and $L v$ is the latent heat of vaporization of the bean moisture, Schwartzberg [1] gives $2790 \frac{\text{kJ}}{\text{kg}}$.

In this balance Equation (3), the heat transfer from hot air to bean $G C p_a [T_{ae} - T_{as}]$, the heat transfer from air to metal parts $Q_{a \rightarrow m}$, the heat transfer from metal parts to beans $Q_{m \rightarrow b}$, the heat production by roasting reactions $Q_r m_{bs}$ and the heat necessary to moisture evaporation at the bean surface during the roasting $L v \left(\frac{dX}{dt} \right) m_{bs}$ are considered. However, in this work, the contact area between coffee beans and metal part is negligible. It is also possible to assume that the heat transfer from hot air to metal is negligible because the temperature of the metal is equal to the air temperature. Under this two hypothesis, the model is simplified as follows:

$$\frac{dT_b}{dt} = \frac{GCp_a[T_{ae} - T_{as}] + m_{bs} (Q_r + Lv \frac{dX}{dt})}{m_{bs}(1 + X)Cp_b} \quad (4)$$

To determine $[T_{ae} - T_{as}]$ in the Equation 4, a balance of air temperature is considered by Schwartzberg [1]. Under the previous hypothesis, it is possible to write:

$$[T_{ae} - T_{as}] = (T_{ae} - T_b) \left(1 - \exp \left[-\frac{\alpha A_{ab}}{GCp_a} \right] \right) \quad (5)$$

where α is the effective air-to-bean heat transfer coefficient ($\frac{W}{m^2 \cdot ^\circ C}$), A_{ab} is the area (m^2) across which air-to-bean heat transfer occurs.

3.5. Properties Estimation

To solve Equation 3 by considering the Equation 5, it is necessary to know α , Cp_b and Q_r .

- *effective air-to-bean heat transfer coefficient*, α , was estimated by the Equation 6 reported by Schwartzberg [1]

$$\alpha = \frac{h_e}{1 + 0.3 \cdot Bi} \quad (6)$$

where, h_e is the heat transfer coefficient at the air-bean surface calculated by the Ranz-Marshall correlation [19] and Bi (Biot number) is used to correct the overall air-bean heat transfer coefficient for heat transfer resistance in the bean.

- *specific heat of the coffee bean*, Cp_b , the values used are obtained by the Equation 7 reported by Schwartzberg [1]

$$Cp_b(1 + X) = 1.099 + 0.0070T_b + 5.0X \quad (7)$$

- *exothermic roasting reaction*, Q_r (rate of exothermic heat production), in $\frac{kJ}{(kg \text{ dry coffee})(s)}$, was calculated using the Equation 8 reported by Schwartzberg [1]

$$Q_r = A \cdot \exp \left[-\frac{H_a}{R_g(T_b(K))} \right] \left(\frac{H_{et} - H_e}{H_{et}} \right) \quad (8)$$

where, H_a is the energy of activation, R_g is the perfect-gas-law constant, A , in $\left[\frac{kJ}{(kg \text{ dry coffee})(s)} \right]$, is the Arrhenius equation prefactor times the amount of heat generated per unit amount of reaction.

Schwartzberg [1] obtained $\frac{H_a}{R_g} = 5500 \text{ K}$, $A = 116200 \left[\frac{kJ}{(kg \text{ dry coffee})(s)} \right]$ and $H_{et} = 232 \frac{kJ}{kg}$.

Measured bean properties:

- $A_{ab} = 1.4 \cdot 10^{-4} \text{ m}^2$ equivalent sphere area
- $m_{bs} = 1.75 \cdot 10^{-4} \text{ kg dry matter}$
- $d_b = 6.6 \text{ mm}$ equivalent sphere diameter

3.6. Temperature and Mass Model Solution

To solve the system of Equations (2-8), we wrote a computer program in *Octave* [13]. This program works in the following way: at instant $t = 0$, we know

- the initial bean temperature $T_b \text{ initial} = 29 \text{ }^\circ\text{C}$,
- the initial bean moisture $X \text{ initial} = 0.105 \frac{\text{kg water}}{\text{kg dry matter}}$,
- the in-air temperature T_{ae} , measured on-line.

These data allow to calculate in time $t = 0$

- ▷ the effective air-to-bean heat transfer coefficient α (Eq. 6),
- ▷ the out-air temperature T_{as} (Eq. 5),
- ▷ the rate of moisture loss $\frac{dX}{dt}$ (Eq. 2),
- ▷ the specific heat of the coffee bean $Cp_b(1 + X)$ (Eq. 7),
- ▷ the rate of exothermic heat production Q_r (Eq. 8).

The set of differential equations was numerically integrated using fourth-order Runge-Kutta method written in *Octave* [13].

3.7. Simulation of the Heat and Mass Transfer

An important characteristic of the model is that *no parameter was adjusted* to describe the bean's temperature and moisture content. The program was written in order to estimate the bean's temperature and moisture content versus time, for a hot air roaster with 25 g of green coffee in different constant air temperatures (T_{ae} from 190 to 300 $^\circ\text{C}$).

Figure 11 shows agreement between experimental and simulated bean's temperature for three roasting temperatures. This three kinetics are representatives for all the experiments. Below 250 $^\circ\text{C}$, the model fits very well the data. For high bean's temperature, the model do not predict the small deviation which we had already observed in the experimental part (Fig. 3b). The deviation can be explained by a beginning of an over-roasting, the exothermic reaction parameters (Eq. 8) given by literature are not valid for this experimental domain. Consequently, the model cannot consider this perturbation. It could be possible to add an other factor to take this phenomena into account, but we preferred to keep a robust model with no adjusted parameter.

The moisture content simulation using Equation (2) leads to acceptable results (Fig. 12) for the beginning of the kinetic. After 300 s the model significantly underestimates the water content. The weight loss include water, volatiles and CO_2 ; the model, which only considers water loss, should give higher results. It would be interesting to measure the water content of the beans during roasting, and to develop a more physical model considering water diffusivity in the bean and mass transfer coefficient between bean and air. But the perturbation of bean's temperature model induced by the bad estimated water loss is negligible. Bean reach the roasting air temperature in less than 180 s, and the moisture content simulation become bad after 300 s of roasting, when the heat transfer is very low.

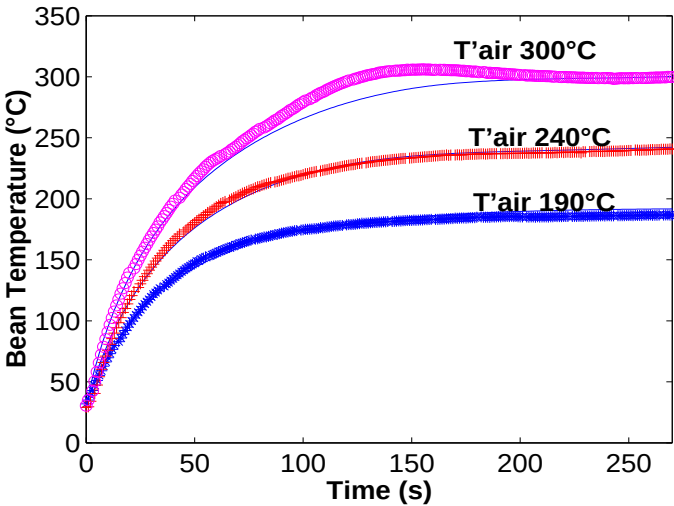


Figure 11. Evolution of the bean's temperature versus time for different air temperatures (*: experimental, -: simulated).

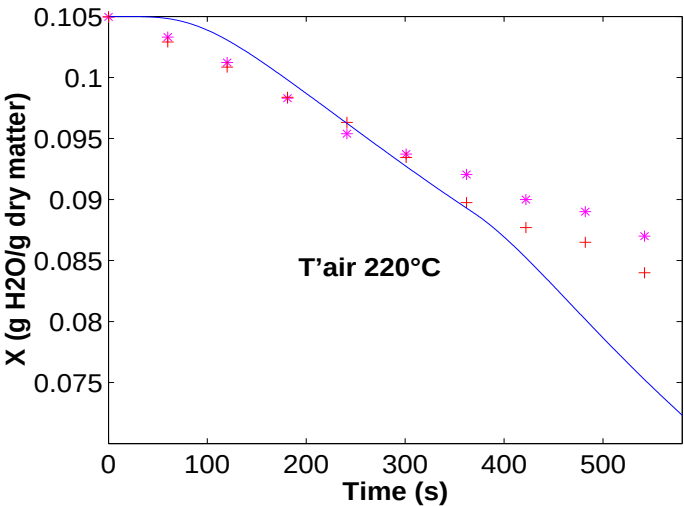


Figure 12. Evolution of the bean's moisture content (*, +: experimental, -: simulated).

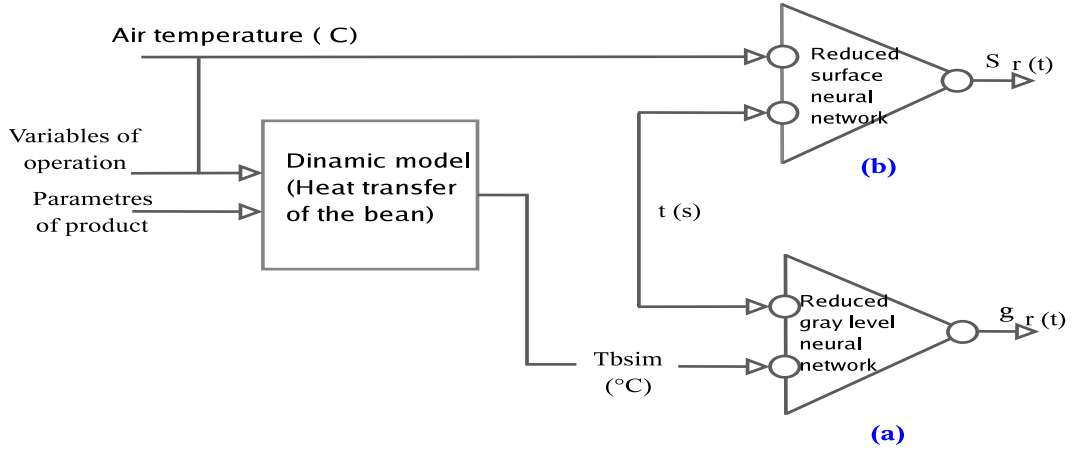


Figure 13. Neural networks, with the roasting time as variable of input.

3.8. Simulation of the Gray and Surface Kinetics

According to obtained experimental data (36 experiments considering 3 repetitions for the gray level, fig. 6) and for the surface (fig. 9). We developed two models, a model for the gray level and the other model for surface. To take into account of the variability of the starting product, the models apply to variables standardized as follows

$$\text{reduced gray}(t) = \frac{ng_t - ng_{t=0}}{ng_{t=0}} ; \quad \text{reduced surface}(t) = \frac{s_t - s_{t=0}}{s_{t=0}} \quad (9)$$

ng_t and $ng_{t=0}$ are gray-level in the time and the initial value, in the same way for the surface s_t et $s_{t=0}$.

According to previous results [5], we planned to use the bean temperature and time as variables of entry for the first model (input variables for the reduced gray-level) and the variables of air temperature and time as variables of entry for the second model (input variables for the projected surface). The best results are obtained from simulated bean temperature by the dynamic model T_b and the time of roasting t (see fig. 13a).

It can also plan to use the experimental bean temperature, but this solution is not realistic at the industrial level because it is very difficult to obtain in a roaster.

For the second model (reduced surface), it was considered the air temperature fixed by the roaster T_a and the roasting time t (fig. 13b).

In order to identify the coefficients of the two models and to validate its, we shared the experimental results in a base of training made up of eight experiments (which are 190, 210, 220, 240, 250, 270, 280 et 300 °C) and a base test composed of four kinetics (200, 230, 260 et 290 °C). Each experiment is made up of three repetitions.

3.8.1. Results and Test of the Two Models

A model of artificial neural network is used to predict the variations of gray level starting from the simulated bean temperature and explicit roasting time. The another predicted

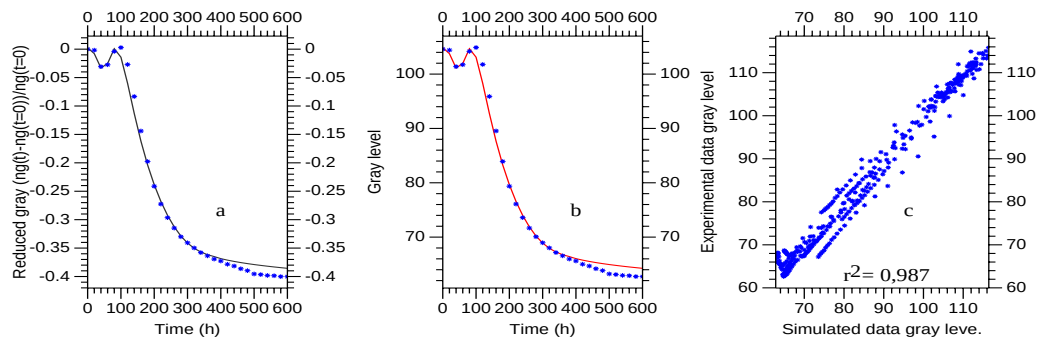


Figure 14. Testing of the neural model for the gray level. (a) reduced gray level function time at air temperature of 260°C : (*) experimental data (-) simulated data with three repetitions. (b) the same reduced gray level converted in gray level : experimental data (*) and simulated data (-). (c) experimental data function of the values simulated for all the base of test.

increase in the surface of the grain, according to the air temperature fixed by the roaster and explicit roasting time.

3.8.2. Gray Level Model

In the phase of training, the best network to predict the gray level comprises 3 neurons in hidden layer. It thus has 13 coefficients (9 weights and 4 bias). To validate this model, we simulated the kinetics contained in the base of test. The evolution of the level of experimental reduced gray for an air temperature fixed by the roaster of 260°C is compared figure 14b, by studying the kinetics of level of gray. This model predicts in a satisfactory way all the curves of the level of gray during roasting with a coefficient of correlation $R^2 = 0.987$. It is important to note that the model predicted well the first phases of the curve (between 0 and 100 seconds) which is complex. Moreover, the layout of all the values simulated according to the experimental data of the base of test (fig. 14c) shows a balanced distribution of the residues. The standard deviation for the base of test is of 0,0229 and for the training of 0,0256. The similarity of these two values shows the predictive capacity of this model.

3.8.3. Surface Model

To predict the surface kinetics of the grain, the best network is similar with the precedent. The Figures 15a and 15b present the evolution of increase in surface experimental and simulated according to time for kinetics contained in the base of test (260 °C). It can note the variation of the surface of the grain during roasting (fig. 15b). The precision of the model is considered to be satisfactory, because the coefficient of correlation is of $R^2 = 0.993$ if the experiments of the two bases are considered. As for the level of gray, the figure 15c compare the values simulated with the experimental values for all the base of test, it shows the capacity to predict the curves of increase in not learned surface. This is confirmed by

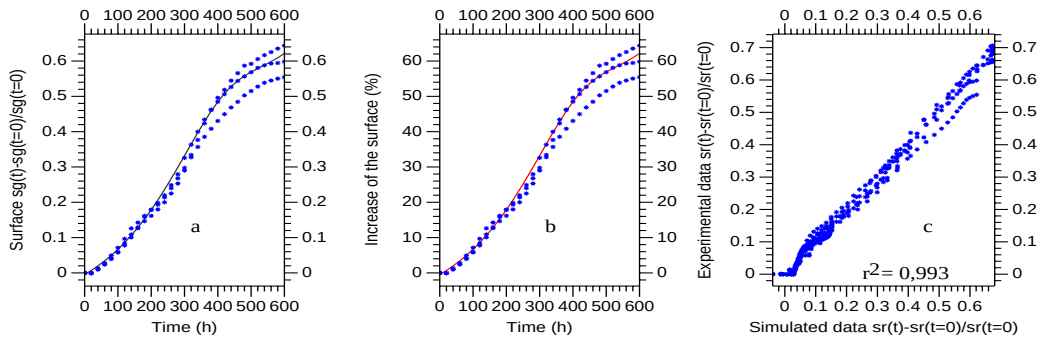


Figure 15. Testing of the neural model for the increase of surface of the bean during roasting. (a) reduced surface function of the time at air temperature of 260 °C : (*) experimental data (with two repetitions) and (-) simulated data. (b) the same reduced surface converted in increased of surface (%) : experimental data (*) and simulated data (-). (c) experimental data function of the values simulated for all the base of test.

the comparable standard deviation on the bases of test (0,022) and of training (0,030).

4. Conclusion

This work propose that it is possible to acquire and traetement of the on-line images during the coffee roasting. This success is due to the programs which work correctly in parallel. In effect, the time of processing for every images is about 4.4 s, and every image is acquired each 20 s. This base of 20 s is sufficient for determine on-line the quality having count the constant of time of roasting. In addition, this work report that the gray level can be an indicator dependable and reliable for the grade of roasting.

The suggested dinamic model can be used in a satisfactory way to describe the behavior of the coffee bean's temperature versus time, in an hot air roaster. This model showed a good agreement with all the experimental kinetics. It is necessary to note that no parameter were adjusted in this model. Furthermore, it can be used to determine how behavior can be affected by parameters variations which are not controlled in the course of roasting. If the parameters are known correctly (αA_{ab} , m_{bs} , X , d_b , Cp_b , V_a and T_{ae}), the model can be used directly, or with small modifications, for other roasting machines where the heat transfer takes place between air and metal and/or a heat transfer of metal towards the bean and the bean towards metal (*i. e. Rotating-drum roaster, Rotating-bowl roaster, Scoop-wheel roaster and Swirling-bed roaster*). Schwartzberg [1] showed that bean's temperature is a good criterion to evaluate coffee quality during roasting process. This temperature is difficult to measure on industrial roaster, but we showed that it is possible to calculate this temperature as a function of input temperature T_{ae} . The model calculates the output air temperature $\widehat{T}_{as}$ at the same time, which is easy to measure on-line. If some perturbation appears, that it is not take into account by the model, the simulated bean's temperature $\widehat{T}_b$, will be wrong, this will appear on the difference between simulated and experimental

temperature ($\widehat{T_{ae}} - T_{ae}$), allowing to adjust the model parameters on-line. Further studies will try to adapt this strategy to industrial roaster.

Two artificial neural networks models are proposed to predict the gray level and the surface of the bean during roasting coffee. These models represent the behavior of these two variables key with a confidence of ($R^2 > 99\%$). These models consider the simulated bean temperature, air temperature fixed by the roaster and roasting time as variables of input. It is important to note that the gray level and surface are two parameters very important to determine the quality on-line. Finally it is possible to obtain the quality of the roasting coffee from these parameters: gray level and surface.

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Chapter 9

MECHANICAL PROPERTIES OF EXTRUDED BIODEGRADABLE FILMS OF NATIVE STARCH AND SUGAR CANE FIBRE

***T. Galicia-García¹, F. Martínez-Bustos^{1*}, O. A. Jiménez-Arévalo²
and E. Aguilar-Palazuelos¹***

¹Ciencia de Materiales, CINVESTAV Querétaro, Apdo. Postal 1-798, Querétaro, Gro., 76230, México. Telephone: (52) 442-4-41-49-05; Fax (52) 442-4-41-49-38

²CIATEQ S. A. de C. V. Querétaro, México. Av. Manantiales No. 23-A, Parque Industrial Bernardo Quintana, C.P. 76246, El Marqués Querétaro, México.

Abstract

The selection of appropriate fibres is determined by the required values of the stiffness and tensile strength of a biodegradable material. Further criteria for the selection of suitable reinforcing fibres are, for example, elongation at failure, thermal stability, and adhesion of fibres at the matrix (starch), dynamic and long-term behaviour, price and processing costs. The fibres can impart synergistic properties to the thermoplastic starch composition. The aim of this research was to study the effects of extrusion variables: feed moisture, barrel temperature and content of sugar cane fibre, starch and plasticizer on the mechanical properties of traction of films that can be used for the manufacturing of disposable bags. Sugar cane fibre (250 µm) and native starch (25% amylose) were used as starting materials. An experimental laboratory single screw extruder with an L/D ratio of 20:1, designed and manufactured by Cinvestav-IPN, México

A screw compression ratio of 1:1, and a rectangular die-nozzle of dimensions 40 mm X 0.75 mm were used. Feeding and die zones temperatures were kept constant at 60 and 75°C respectively; whereas the temperature of the transition zone (zone 2) was set according to the experimental design (110-140°C). The screw speed was kept constant at 40 rpm. The extruded films were stored for 40 h under controlled temperature and humidity (23±2°C and 50± 5%) for further analysis. The evaluated properties of traction were: Maximum resistance to the traction ($\sigma_{\max}$), Elongation at fracture (ϵ_f); and Modulus of elasticity (E) according to standard ASTM-D882-00. It was found that high plasticizer content (>30%) decreased the $\sigma_{\max}$. On the

* E-mail address: fmartinez@qro.cinvestav.mx

other hand, intermediate fibre content (5-15%) increased the $\sigma_{\max}$; high barrel temperatures (130°C) and intermediate fibre contents favored the ε_f and therefore resulted in thinner films. Also, high fibre contents (>15%) and low feed moisture (18.25%) decreased E which resulted in a less flexible film. The best conditions for thermoplastic extrusion were found to be: Barrel temperature (110-130°C), feed moisture (20.5-22.75%), fibre content (5-15%) and plasticizer (22-30%) as shown in assays 3, 5, 7, 8, 11, 12, 15, 16, 25, 30. In summary, fibres can impart more strength to the starch-bound matrix without adding significantly bulk or mass to the matrix. Sugar cane fibre in blends with native starch improved the strength and other mechanical properties of the films, and it has strong potential for the production of disposable bags.

Introduction

The plastics are generally elaborated from compounds well-known as polymers. The main polymers used in the elaboration of supermarket bags are the high and low density polyethylene of (HDPE, LDPE) and the polypropylene (PP) (Rubin 1998). The trade bags have a great efficiency; a small supermarket bag that weighs among 5-7 g can take a load of up to 10 kg of products, which represents approximately 1700 times its own weight. Also these bags have the advantages of fast and safe packing of products, as well as their transportation to home, so a fast growing of these products has been promoted (CIT 2001). Although the trade bags are used commonly for a variety of purposes at home and in some establishments (INIT 2005), these products generate enormous problems of contamination due to the short time of using, becoming wastes that are later incorporated to sanitary fillers. These plastics take about 150 years to degrade and reintegrate to the environment (Agusti 2004). Mexico and many Latin America countries do not have an effective system of management; almost 40 millions of tons of solid residues are annually generated and approximately 2.5 million tons are plastics (INEGI 2006) that aggravate health, social, economic and environmental problems (CMIA 2003).

Polymers

The polymers are macromolecules that are characterized by their size, chemical structures, intra and intermolecular interactions, for their physicochemical nature and repetitive units in their chains and distinctive characteristics between them (Morton-Jones 1997). The polymers can be classified according to: a) their origin (natural, artificial), b) polymerization mechanism (addition, condensation), c) structure (lineal, network), d) mechanical behavior (elastomers, plastics, fibres) and e) melting and/or solubility (thermoplastics, thermorigid) (Bilmeyer 1984).

Biodegradable Polymers

The biodegradable polymers constitute an emergent field of the science and technology; they are defined as organic materials with molecular degradation, generally in watery atmosphere, result of complex action of organisms (ISO-478 1995). The production of biodegradable biopolymers of commercial application has been reported (CIT 2005): Biopol (PHB),

Pululano, polylactic acid (PLA) and others, derived from corn starch by fermentative processes, however, they are biodegradable only under appropriate physiochemical conditions of humidity, temperature, acidity, microorganisms inoculation, blend composition, etc. (INTI 2005). Due to their low cost and high availability the natural polymers have great importance because they can be used as substitutes of synthetic commercial polymers. Factors such as greater environmental awareness, societal concern and the depletion of petrochemical resources together provide an impetus to drive the growth of new materials and products based on natural fibres and biopolymers. Waste disposal is becoming increasingly important with the recognition that landfill is not sustainable and as such costs are increasing, with more responsibility being placed on producers.

Starch

Starch is a product of low cost and abundant in nature in a wide variety of environments, it is completely biodegradable and it can be used as matrix of degradable products for specify necessities of the market (Fábio et al 2004). The starch is essentially a homopolymer of D-glucose in its more stable conformation. Glucose polymerization in starch results in two types of polymers, amylose and amylopectin. Amylose is an essentially linear polymer, whereas the amylopectin molecule is larger and is branched. Amylose is considered to be an essentially linear polymer composed almost entirely of α -1,4-linked D-glucopyranose. The interior of the helix contains hydrogen atoms and is therefore hydrophobic. Amylopectin, the predominant molecule in most normal starches, is a branched polymer that is much larger than amylose. Amylopectin is composed of α -1,4-linked glucose segments connected by α -1,6-linked branch points. It has been estimated that about 4-6% of the linkages within an average amylopectin molecule are α -1,6 linkages. The ratio of amylose and amylopectin contents in the starch granule contribute to important differences in starch properties and functionality (Whistler et al 1984). The thermoplastic starch is strongly hydrophilic, can be used as matrix of biodegradable materials or in a partial substitution of some components in traditional plastics. The mechanical properties of the films from starches are generally inferior to those of synthetic polymers, however, when a plasticizing agent as water is added, these materials improve their mechanical properties (Cha and Chinnan 2004). The mechanical behavior of thermoplastic materials produced with starch is related to moisture content of the material; the water within the starch exerts a function of plasticizing, which allows to decrease the glass transition temperature (T_g) and melting point, making possible starch processing at temperatures below that of starch decomposition.

Natural Fibres

Recently, the interest to find new uses for natural fibres is growing due to the high production of agricultural residues and agroindustrial co-products. In México and some Latin America countries large volumes of fibre are available principally from corn, sorghum, wheat, bagasse, coconut, yute, agaves, pineapple husk and some wild grass. Mexico harvested in 2004 (from January to August) more than 45,000,000 tons of sugar cane that generated approximately 7, 000,000 tons of fibre. These materials are available, renewable, biodegradable, recyclable,

of low cost and are a suitable source of fibre of industrial interest (INEGI 2006). Diverse researchers (Bledzki 1999, Amash 2000, Funke 1998) have reported that the use of cellulose fibres as reinforcement material in thermoplastic matrices, as well as its use in thermoplastic starches increased the force of tension. The lignocelluloses material is constituted by cellulose, lignin and hemicellulose in an approximate relationship of 4:3:3 varying sensibly between the different species (Fengel and Wegener 1984, Sjöström 1981, Misra 1993, Oggiano 1997). The cellulose is a lineal polymer conformed by units of β -(1-4)-D-glucopyranose. The hemicellulose is defined chemically as a polysaccharide constituted by a chain linkage of (1-4) β -D-piranoose (xilose) as well as residues in the chain formed mainly of D-manose, D-galactose, D-arabinose and uronic acids. Due to its hydrophilic nature hemicellulose can be used in hemicellulose/starch mixtures (Gáspar et al 2005). Stanislaw et al (2003) reported that high fibre concentrations (>50%) in a starch-water system delayed the glass transition phase, and required more water and heat to stabilize the system. Classical synthetic fibres reinforced polymers often cause considerable problems in terms of reuse or recycling at the end of their lifetimes. This is primarily because the compounds consist of very stable fibres and matrices. Additionally, technical benefits of natural fibres such as low density, high toughness, acceptable specific strength properties, ease of separation, enhanced energy recovery, carbon dioxide sequestration and biodegradability will all act to drive the growth of markets based on biopolymers. Furthermore, the desire to promote the use of crops grown for industrial, non-food purposes is driving the uptake of novel materials.

Plasticizing Agents

The plasticizing agents are additives frequently used in some types of polymeric materials, with the objective of improving processability and to increase the flexibility and extensibility, inducing changes in the physiochemical and mechanical properties. The plasticizing agents are compounds of low volatility that can be solid or commonly liquids of high molecular mass (Kester and Fenema 1986). The basic requirements for a plasticizing agent are: a) compatibility with the components in the formulation of the polymeric material, indicating the existence of similar intermolecular forces between the two components and b) null volatility. The mechanism of action of the plasticizing agent consists on a decrease in the intermolecular forces between adjacent polymeric chains, it makes that the plasticizing agent acts as lubricant allowing the macromolecules freely slip some over other. The types of plasticizing agent can affect the mechanical properties, since they cause a decrease of the cohesion and tension forces, the glass transition temperature and melting temperature, however, the plasticizing does not alter the chemical nature of the macromolecules (Guilbert 1986). The effect of the glycerol content has been evaluated on the mechanical and rheological properties of extruded corn starch and its relation with the change in the glass transition temperature in the production of new biodegradable plastics (Yu et al 1998). The reports indicated that the glycerol is an excellent plasticizing agent for starch and improves in a great extent its technological properties. An increasing in the glycerol content decrease the values of apparent viscosity, resistance to the tension and the melting and glass transition temperatures, although, increase the percentage of elongation.

Thermoplastic Extrusion

There is great interest in the potential of thermoplastic extrusion in terms of future growth in biopolymers application in the industrial sector. Diverse researchers have reported that the extrusion process can be use in an effective way for the elaboration of plastic materials as the elaboration of packing and biodegradable films from renewable sources with mechanical characteristics that fulfill the established norms (Lourdin et al 1995, Bader and Göritz 1994, Avérous et al 2001, Sebio 2003).

The basic principle of the extrusion process is the transformation of a solid material into a fluid by the application of heat and mechanical work, promoting the melting of starch. (Morton-Jones 1997, Dziekak 1989). The extruders offer important advantages related to other industrial processes, such as a reduction of the processing time, energy and costs, large-scale continuous production, high production capacity for unit of area and absence of effluents (Stanley 1986). Natural starch is a readily available and inexpensive material. Therefore, attempts have been made to process natural starch on typical equipment using existing technology known in the plastic industry. However, since natural starch generally has a granular structure, it needs to be plasticized and/or otherwise modified by extrusion before it can be melt-processed like a thermoplastic material. The thermoplastic starch is strongly hydrophilic and can be used as matrix of biodegradable materials or in a partial substitution of some components in traditional plastics. The mechanical properties of the films from starches are generally inferior to those of synthetic polymers, however, when is added a plasticizing agent, as water, these materials improve their mechanical properties (Cha and Chinnan 2004). The mechanical behavior of thermoplastic materials produced of starch is related with the moisture content of the material, due to that the water presents in starch exerts a function of plasticizing, which allows to decrease the glass transition temperature (T_g) and melting point and thus, possibility its processing at temperatures below these of starch decomposition. By means of the extrusion process can be produce films and sheets. In the die design for the production of sheets or films it is necessary to modify the fundamental cylindrical form of the melted material as go into the die area until achieving a thin form, more wide as well as and to maintain uniform the existent heat, and the profiles of pressure and temperature (Morton-Jones, 1997).

Mechanical Properties

In general the mechanical properties included the complete properties that determine a response from the material to the application of a mechanical external work. These properties are manifested by the capacity of the materials to develop reversible or irreversible deformations. These characteristics of the materials are generally evaluated using approved methods that measure the responses of the materials that indicate diverse tension-deformation dependences. The traction properties are useful for the identification and characterization with application in development, and in the specification and evaluation of the quality of the materials (ASTM D882-00 2001). Between these properties are considered: a) Maximum resistance to the traction (σ_{max}), it is the maximum resistance offered by the material when it is submitted to traction, b) Tensile strength (ϵ_f), it represents the ratio among the elongation of the test body and their initial body, and c) modulus of elasticity (E), it is a ratio between the

traction tension and deformation inside the elastic limits where the deformation is completely reversible and proportional to the tension.

The aim of this work was to evaluate the effect of the extrusion variables: feed moisture, barrel temperature and blend formulations, in mechanical properties of biodegradable films according to the established experimental designs.

Materials and Methods

Materials

Native (25% amylose) corn starch was purchased from Almex (Mexico D.F). Bagasse was donated by sugar cane factories from Veracruz State, (Mexico), Glycerol was acquired from Sigma-Aldrich (Germany). The sugar cane fibres were cleaned, sun dried for 48 h and milled in a hammer Pulvex mill (Pulvex, model 200, Mexico) using a mesh sieve with orifices of size of 0.5 mm of diameter. The fibres were sifted (Rotap, RX - 29 - Tyler Inc., USA) and those of intermediate size (mesh 40 and 60) were separated and refrigerated at 5°C for 12 h for further use.

Extrusion Process

An experimental laboratory single screw extruder (Cinvestav-Qro, Mexico) with an L/D ratio of 20:1, a screw compression ratio of 1:1 at 30 rpm, and a rectangular die with internal measurements of 40 mm x 0.75 mm long was used. Barrel temperatures in the feeding and final zones were kept constant at 60 and 75°C respectively; whereas, the barrel temperatures of the second zone varied from 110 to 140°C according to the experimental design (Table 1). The three heating zones were independently electrically-heated, and air-cooled. Feed moisture (FM) varied from 16% to 30%, the feed rate varied according to the weight of the sample, and the screw speed was 40 rpm.

Characterization of Films

The samples were stored in desiccators at room temperature (25°C) for 12 h (ASTM D882-00), with saturated saline solutions at temperature of $23 \pm 2^\circ\text{C}$ and relative humidity of $50 \pm 5\%$, for 40 h for further mechanical test according to the methodology of Kitic et al (1986).

Mechanical properties of films.

Mechanical properties of traction (tests of tension deformation)

Mechanical properties were evaluated according to the ASTM-D882-00 and following the modifications made by Gnanasambandam et al (1997).

The samples test was carry out in an universal TA–XT2 Texture Analyzer (Texture Technologies Corp., Scarsdale, NY, USA/Stable Micro System, Godalming, Surrey, UK)

with two claws for tension test (TA-96) with a distance between claws was of 83 mm, keeping 5% of each end of the sample in a claw. Ten repetitions were registered by each sample using a computer interface to data record. The traction properties measured were the following:

a) Maximum resistance to the traction ($\sigma_{\max}$): It is the ratio between the maximum measured force and the initial transversal area of the test body and expressed in MPa or N/m².

$$\text{Maximum resistance to the traction (MPa)} = F_{\max} / A_0$$

Where: $F_{\max}$: Maximum registered force (N); A_0 : Initial minimum area of the body test.

b) Elongation at fracture (ϵ_f): it represents the ratio among the maximum elongation of the test body and their initial body

$$\epsilon_f (\%) = (A_t / DG) * 100$$

Where:

A_t : total elongation of the body test after of the breaking (m)

DG: initial distance between claws (m).

c) Modulus of elasticity (E): Lineal relation of the tension curve versus the deformation of the body test or growing elongation and proportional to the deformation (elastic region). It is expressed in MPa or N / m².

$$\text{Modulus of elasticity (MPa)} = (F_i / A) * (DG / A_i)$$

Where:

F_i : It is the localized force in the high lineal region of the curve

A: Initial mean area of the body test (m²)

A_i : Elongation of the body test in the lineal region of the curve

DG: initial distance between claws (m)

Statistical analysis

Experimental Design

The values of the variation levels, the code as well as the design statistics used (Table 1) were analyzed using a factorial design 2⁴ increased with 8 axial points and 6 central points to 30 experimental units. The repetitions in the central point allowed the estimation of the variability. All assays were performed randomly (Table I) and the data was analyzed by response surface methodology (Hill and Hunter 1966).

The levels of the independent variables were determined according to preliminary tests. The levels were coded in the following way:

Independent Variables:

X_1 = BT = Barrel temperature ($^{\circ}\text{C}$)

X_2 = FM = Feed moisture (%)

X_3 = G = Plasticizing agent; glycerol (%)

X_4 = F = Fibre (%)

The experimental data were used to determine the coefficients (β_0) in the equation of expansion of Taylor series (quadratic polynomial) and the general expression is:

$$Y_i = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \varepsilon$$

where: Y_i is the generic response function and X_1 , X_2 , X_3 and X_4 the independent variables. β 's are the estimated coefficients and ε is the residue that measure the experimental error. The probability of F (p of F), and the influence of the variables were registered using the response surface graphics.

The response variables were: Maximum resistance to the tension, RMT (Mpa); tensile strength, BE (%); and Modulus of elasticity, E (Mpa).

Analysis of Data

The preliminary data were analyzed using response surface methodology, applying the statistical package Design-Expert (Stat-Ease 2003) version 6.1.0. A polynomial of second order was used to predict the experimental behavior.

Results and Discussion

Maximum resistance to the traction ($\sigma_{\max}$), Elongation at fracture (ε_f) and modulus of elasticity (E), showed a significant prediction model ($p \leq 0.05$). These tests were useful to characterize and to evaluate the mechanical properties obtained in the polymeric materials.

Table 1. Experimental design

Assay	Codified variables ^a				Decodified variables ^b		
	BT (X ₁)	FM (X ₂)	G (X ₃)	F (X ₄)	$\sigma_{\max}$	ε_f	E
1	110	18.25	22.25	5.00	0.904	3.538	46.170
2	130	18.25	22.25	5.00	1.027	4.003	46.565
3	110	22.75	22.25	5.00	0.760	3.818	31.199
4	130	22.75	22.25	5.00	1.224	5.233	43.164
5	110	18.25	30.75	5.00	0.358	2.744	18.619
6	130	18.25	30.75	5.00	0.424	3.016	17.384
7	110	22.75	30.75	5.00	0.344	2.699	16.884
8	130	22.75	30.75	5.00	0.515	3.393	21.142
9	110	18.25	22.25	15.00	1.258	1.872	115.071
10	130	18.25	22.25	15.00	0.429	1.581	42.723
11	110	22.75	22.25	15.00	0.253	1.336	34.997
12	130	22.75	22.25	15.00	0.528	1.944	52.039
13	110	18.25	30.75	15.00	0.386	1.454	40.206
14	130	18.25	30.75	15.00	0.321	1.328	38.796
15	110	22.75	30.75	15.00	0.263	1.519	27.041
16	130	22.75	30.75	15.00	0.375	1.657	37.239
17	100	20.50	26.50	10.00	0.323	1.474	34.710
18	140	20.50	26.50	10.00	0.283	1.758	24.372
19	120	16.00	26.50	10.00	0.476	1.521	48.420
20	120	25.00	26.50	10.00	0.425	2.263	29.487
21	120	20.50	18.00	10.00	0.437	1.939	37.096
22	120	20.50	35.00	10.00	0.181	1.224	20.139
23	120	20.50	26.50	0.00	0.285	4.261	8.739
24	120	20.50	26.50	20.00	0.228	2.330	23.526
25	120	20.50	26.50	10.00	0.272	1.962	21.808
26	120	20.50	26.50	10.00	0.304	1.966	24.727
27	120	20.50	26.50	10.00	0.294	2.299	16.626
28	120	20.50	26.50	10.00	0.251	2.454	17.035
29	120	20.50	26.50	10.00	0.279	2.424	19.572
30	120	20.50	26.50	10.00	0.236	1.899	21.640

^aBT= Barrel temperature (°C); FM= Feed moisture (%); G= Glycerol (%); F= fibre (%);

^b $\sigma_{\max}$ = Maximum resistance to the traction (MPa), ε_f = Elongation at fracture (%);

E= Modulus of elasticity (MPa).

Models of Prediction

Maximum Resistance to the Traction ($\sigma_{\max}$).

The experimental values of the biodegradable films obtained by the extrusion process varied from 0.18 to 1.2 MPa (Table 2). The regression analysis showed that $\sigma_{\max}$ was affected by G

($p \leq 0.002$), F ($p \leq 0.109$), FM-FM ($p \leq 0.106$) and BT-FM ($p \leq 0.071$). The prediction model for $\sigma_{\max}$ used the coded variables:

$$Y_{\sigma_{\max}} = 0.40 + 9.8 \text{ E-}3 * X_1 - 0.04 * X_2 - 0.16 * X_3 - 0.077 * X_4 + 0.072 * X_2 * X_2 \\ + 0.11 * X_1 * X_2 - 0.083 * X_1 * X_4$$

Using original variables:

$$Y_{\sigma_{\max}} = 17.54880 - 0.080690 * BT - 1.17224 * F - 0.038314 * G + 0.18388 * F \\ + 0.014129 * FM^2 + 4.79473 \text{ E-}003 * BT * FM - 1.66140 \text{ E-}003 * BT * F$$

The prediction model explained 52.57% of the total variation ($p \leq 0.0115$) for the values of $\sigma_{\max}$ (Table 2).

Figure 1 shows the effect of the interaction BT-FM where the maximum values of $\sigma_{\max}$ (0.866 MPa) were at BT of 130°C, FM=22.25%, G=22.25% and F=5%. However, at high BT and FM (130°C and 22.25%, respectively) and low G (5%) the increase of glycerol content in the blend decreased the values of $\sigma_{\max}$ (0.536 MPa). Low G values (22.25%) and high contents of F (15%) $\sigma_{\max}$ showed the maximum values (0.757 MPa) at BT (110°C) and FM (18.25%).

In a general way the values of $\sigma_{\max}$ were favored at low values of G and F. The increment of G values decreased drastically $\sigma_{\max}$. Thus, high contents of G originated flexible films, however, with a low resistance to the tension as showed in assay 22 (BT120°C/FM20.5%/G35%/F10%). Jansson et al (2005) reported that films added with high glycerol contents in blends with starch induced a drastic decrease in the tension strength, increasing the elongation at fracture (ϵ_f) until 35%. However, the increasing of F until 15% and at high G contents increased the $\sigma_{\max}$ values (assays 10,12,19,20 and 21). Similarly Funke et al (1998) and Dufresne and Vignon (1998) reported that considerable improvements in product properties were achieved by adding small amounts of fibres to the starch samples with natural plasticizers. Blend systems with 2-7% fibres resulted in an increase of tensile strength and water resistance of these products (Funke et al 1998).

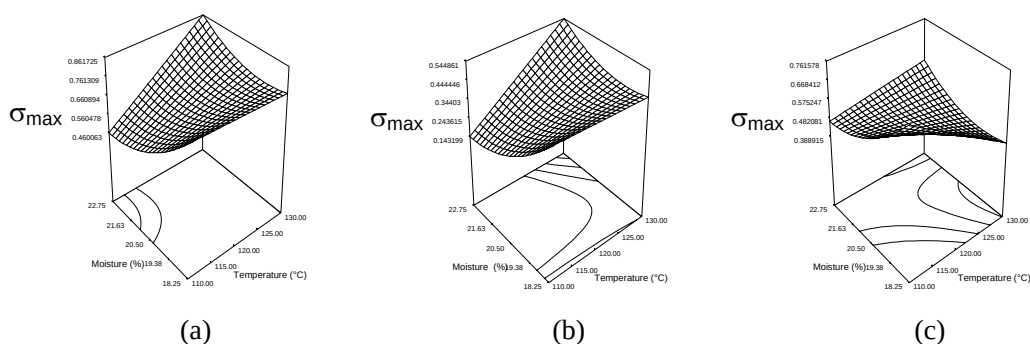


Figure 1. Effect of the interaction barrel temperature-feed moisture in Maximum resistance to the traction ($\sigma_{\max}$). a) G-F (low concentrations), b) with an increasing of G, c) with an increasing of F.

Analyzing the effect of the interaction BT-F (Figure 2) the maximum values of $\sigma_{\max}$ (0.759 MPa) showed a wide range of F and BT (5-15% and 110-130°C, respectively).

Whereas at low FM (18.25%), and G (22.25%), the values of $\delta_{\max}$ (0.496 MPa) were decreased with an increasing of BT and FM. By other hand an increasing of FM resulted in the maximum values of $\sigma_{\max}$ (0.864 MPa) at high BT (130°C), low F (5%) and G (22.25%).

The minimum values of $\sigma_{\max}$ (0.182 MPa) resulted with an increasing of G (15%) at BT of 130°C. In a general way the values of $\sigma_{\max}$ were increased with a decreasing of G and an increasing of FM and also at high values of BT and low FM. Thus, the $\sigma_{\max}$ values were favored at 15% of fibre and intermediate G values (18.25 and 22.25%).

The incorporation of cellulose fibre acts as reinforcement in thermoplastic materials (Averous et al 2001). This evidence was demonstrated in the assay 23 where the absence of F decreased the $\sigma_{\max}$. According to Stanislaw et al (2003) high fibre contents decreased the $\sigma_{\max}$ forming a rigid and fragile material.

The $\sigma_{\max}$ of the films determines the final quality of the bags and is an indicator of the high posterior behavior of the films during thermoformed process.

Table 2. Coefficients regression and variance analysis of the first order equations (prediction models).

Coefficients	Maximum resistance to the tension	Elongation at fracture	Modulus of elasticity
	$Y \sigma_{\max}$	$Y \varepsilon_f$	$Y E$
Interception			
β	0.40	2.17	20.23
Lineal			
β_1	9.88E-3 _{NS}	0.16 *	-2.16 _{NS}
β_2	-0.040 _{NS}	0.15*	-5.82 **
β_3	-0.16 ***	-0.29 ***	-9.52 ***
β_4	-0.077 *	-0.82 ***	7.36 ***
Quadratic			
β_{11}		-0.059 _{NS}	4.16 *
β_{22}	0.072 *	0.010 _{NS}	6.52 **
β_{33}		-0.067 _{NS}	3.93 *
β_{44}		0.36 ***	0.81 _{NS}
Interactions			
β_{12}	0.11 *	0.16 _{NS}	7.38 **
β_{13}		-0.076 _{NS}	3.42 _{NS}
β_{14}	-0.083 *	-0.16 _{NS}	-3.87 _{NS}
β_{23}		-0.038 _{NS}	4.78 _{NS}
β_{24}		-0.10 _{NS}	-4.32 _{NS}
β_{34}		0.25 **	-0.53 _{NS}
R^2	0.5257	0.8817	0.7398
$P \leq$	0.0115	0.0001	0.0201

*Significance Level to $p \leq 0.10$; ** Significance Level to $p \leq 0.05$; *** Significance Level to $p \leq 0.01$

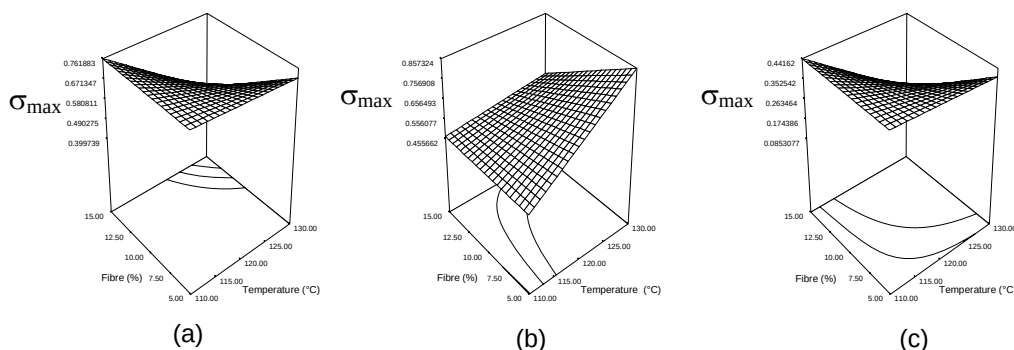


Figure 2. Effect of the interaction barrel temperature-fibre in maximum resistance to the tension ($\sigma_{\max}$). a) FM-G (low concentrations); b) with an increasing of FM; c) with an increasing of G.

Elongation at Fracture (ϵ_f)

The experimental values of the analysis of biodegradable films varied in a percentage from 1.22 to 5.23 (Table 1). The regression analysis showed that ϵ was affected by G ($p \leq 0.009$), F ($p < 0.001$), F-F ($p \leq 0.001$), and G-F ($p \leq 0.055$). The prediction model for the ϵ used the codified variables:

$$Y_{\epsilon f} = 2.17 + 0.16 * X_1 + 0.15 * X_2 - 0.29 * X_3 - 0.82 * X_4 - 0.059 * X_1 * X_1 + 0.010 * X_2 * X_2 - 0.067 * X_3 * X_3 + 0.36 * X_4 * X_4 + 0.16 * X_1 * X_2 - 0.076 * X_1 * X_3 - 0.16 * X_1 * X_4 - 0.038 * X_2 * X_3 - 0.10 * X_2 * X_4 + 0.25 * X_3 * X_4$$

Using original variables:

$$Y_{\epsilon f} = 0.51069 + 0.091368 * BT - 0.66613 * FM + 0.31011 * G - 0.19907 * F - 5.88352E-4 * BT * BT + 2.01818E-3 * FM * FM - 3.73168E-3 * G * G + 0.014445 * F * F + 7.04307E-3 * BT * FM - 1.79229E-3 * BT * G - 3.14632E-3 * BT * F - 3.99772E-3 * FM * G - 9.01491E-3 * FM * F + 0.011662 * G * F$$

The used prediction model explained 88.17% of the total variation ($p \leq 0.0001$) for the values of ϵ_f (Table 2). Figure 3 shows the effect of the interaction G-F, where the maximum value of ϵ_f (4.60) was found at high barrel temperature (130°C) and FM (22.75%), and at low F (5%) and high G (26%).

The decreasing of BT in great extent did not modify the values of ϵ_f (3.8-4.0%). However, when the FM decrease the change in the values of ϵ_f were noticeable (4.1-3.7%).

In a general way the values of ϵ_f were decreased with a decreasing of FM and high BT (130°C) and intermediate fibre contents ($< \text{ or } = 15\%$) that resulted in thin films. By other hand, high concentrations of F could induce adverse effects modifying the velocity of the flow of the material inside of the extruder, resulting in an irregular material and also, favoring the separation of the phases (starch-glycerol and fibre). The films without fibre (assay 23) had a

thickness higher than 1mm, thus the use of fibre at intermediate values improved the tension and increased the ϵ_f values.

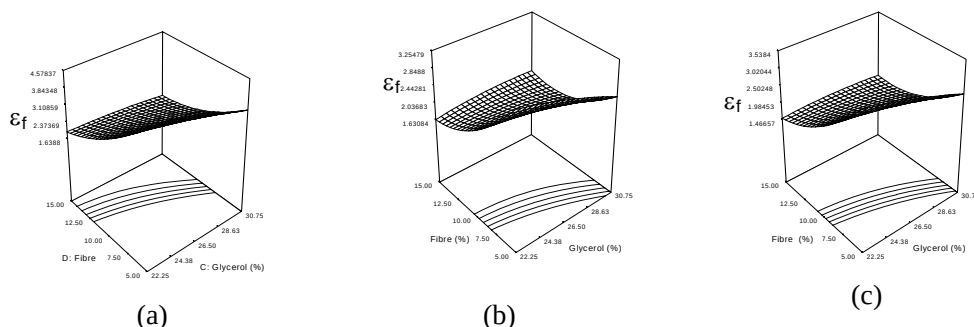


Figure 3. Effect of the interaction glycerol-fibre elongation at fracture (ϵ_f) a) FM-BT (at high concentrations), b) decreasing BT; c) decreasing FM.

Modulus of elasticity

Modulus of elasticity (E). The experimental values of biodegradable films varied from 8 to 115 MPa (Table 1). The regression analysis showed that E was affected by FM ($p \leq 0.055$), G ($p < 0.004$), F ($p \leq 0.019$), FM-FM ($p \leq 0.025$), BT-FM ($p \leq 0.048$). The prediction model for E used the following codified variables:

$$Y_E = 20.23 - 2.16 * X_1 - 5.82 * X_2 - 9.52 * X_3 + 7.36 * X_4 - 4.16 * X_1 * X_1 + 6.52 * X_2 * X_2 + 3.93 * X_3 * X_3 + 0.81 * X_4 * X_4 + 7.38 * X_1 * X_2 + 3.42 * X_1 * X_3 - 3.87 * X_1 * X_4 + 4.78 * X_2 * X_3 - 4.32 * X_2 * X_4 - 0.53 * X_3 * X_4$$

Using original variables:

$$Y_E = 2596.25002 - 18.28943 * BT - 104.10729 * FM - 33.43105 * G + 18.64211 * F + 0.0416274 * BT * BT + 1.28707 * FM * FM + 0.21767 * G * G + 0.032422 * F * F + 0.32795 * BT * FM + 0.080525 * BT * G - 0.077375 * BT * F + 0.49953 * FM * G - 0.38407 * FM * F - 0.024938 * G * F$$

The used prediction model explained 73.98% of the total variation ($p \leq 0.0201$) for the values of E (Table 3). Fig. 4 shows the effect of the interaction BT-FM where the maximum value of E (71.43 MPa) was attained at low FM and BT (18.25% and 110°C, respectively), and at low G (22.25%) and high F (15%).

The increasing of G content decreased the values of E and these values were increased (35.09 MPa) with a decreasing of F, at high values of FM (22.75%) and BT (130°C). Moraru et al (2002) reported that high values of FM and G favored the E values; however, at low contents of FM the material could develop high rigidity. In agreement, the assay 9 of this work, where low values of BT, FM, G, and high values of F resulted in a rigid material. Thus, the E values indicated the flexibility of the materials.

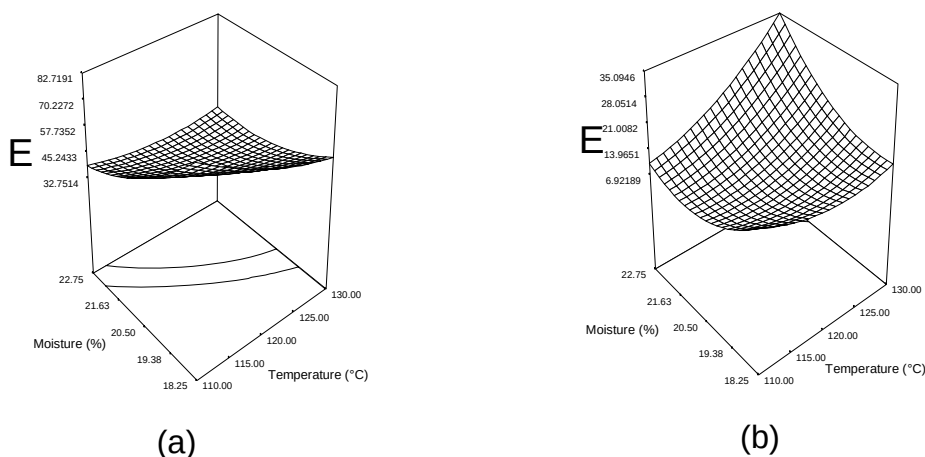


Figure 4. Effect of the interaction barrel temperature-feed moisture in the modulus of elasticity (E).

Conclusions

The use of high glycerol contents (> 30%) decreased the mechanical resistance to the traction ($\delta_{\max}$); also, high fibre contents, not more than 15%, increased the $\delta_{\max}$ values at low barrel temperatures. Thin films with low tensile strength were found at high barrel temperatures (130°C) and intermediate fibre contents (not more than 15%); also low concentrations of glycerol (18%) inhibited the stretching of the material. The modulus of elasticity was decreased with high fibre contents (> 15%) and low feed moisture (18.25%). The use of high fibre contents (20%) difficult the processing of the material inside the extruder and induced its separation from the rest of the components. Acceptable films for the elaboration of bags in a posterior thermoformed step were found. The best extrusion conditions were found for the assays 3,5,7,8,11,12,15,16,25 and 30, at barrel temperatures from 110 to 130°C, feed moisture from 20.5 to 22.75%, fibre content from 5 to 15%, and glycerol content from 22 to 30%. Extruded films from fibre and starch showed improved mechanical properties and performance characteristics for the fabrication of disposable bags.

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Chapter 10

POTENTIALITY OF SOME NATURAL FIBRES AND NATIVE STARCH FOR MAKING BIODEGRADABLE MATERIALS

***E. Aguilar-Palazuelos¹, F. Martínez-Bustos^{1*}
O. A. Jiménez-Arévalo², T. Galicia-García¹
and J. A. Delgado-Rangel^{2,3}***

¹Ciencia de Materiales, CINVESTAV Querétaro, Apdo. Postal 1-798, Querétaro, Qro., 76230, México.

²CIATEQ S. A. De C. V. Querétaro, México. Av. Manantiales No. 23-A, Parque Industrial Bernardo Quintana, C.P. 76246, El Marqués Querétaro, México.

³Facultad de Química, Universidad Autónoma de Querétaro, Apdo. Postal 184, Querétaro, Qro. 76010, México.

Abstract

Diverse formulations of thermoplastic biopolymers have been developed in an attempt to at least partially replace non-degradable petroleum-based products with biodegradable components which can be used for the manufacture of extruded and/or moulded articles such as films, utensils, containers, electric appliances and automobile interior materials. Several of these materials have been formulated of blends of starch and other components. In general, such thermoplastic biopolymers that have been developed primarily for the packaging industry do not have the mechanical characteristics of conventional polymers. In particular, the high rigidity and fracturability are disadvantageous for this projected usage. In addition, these materials tend to interact among them, this causes that the materials loss their dimensional stability, and tear or collapse. In an attempt to improve the structural stability of articles made from starch-based compositions, our experimental research have shown the viability of the use of natural fibres as reinforced materials in blends with native corn starch. The use of starch blended with agricultural fibres result attractive because the final products have the advantages of low cost, low density, acceptable specific strength properties, and biodegradability. Also, in many Latin American countries there are available high volumes of

* E-mail address: fmartinez@qro.cinvestav.mx. Telephone: (52) 442-4-41-49-05; Fax (52) 442-4-41-49-38

agricultural residues that can be used as raw materials to fabricate biodegradable materials. In this work, the effect of fibre and glycerol contents in blends with native corn starch on structural and mechanical properties of extruded injected-moulded plates was evaluated. Mechanical properties (elasticity modulus), structural properties (X-ray diffraction, viscosity profiles, infrared spectroscopy, scanning electronic microscopy) and biodegradable properties were evaluated in extruded injected-moulded plates. These plates showed better mechanical properties when increasing the fibre content, improving their resistance. Also, increasing the glycerol content improved the elongation and processability in plates. Structural properties (X-ray diffraction), viscosity profiles, infrared spectroscopy and scanning electronic microscopy (SEM) showed some changes in the physical structure of the materials as well as the possible interaction of fibres with the polymeric starch matrix. Studies of biodegradation showed that the fabricated plates were completely biodegradable. The best mechanical properties of the plates were those that had a formulation of 10% of fibre and 10% of glycerol with starch. It becomes clear that some of these natural fibres can potentially be used as reinforced material in blends with native starch with similar characteristics to those fabricated with conventional polymers.

I. Introduction

In the last 60 years, the synthetic polymers have experienced a progressive growth, constituting an important area in the polymers science. During this period these materials have invaded almost all human activities. This fact is due to their low cost, repeatability at high velocity of production and its durability, and high resistance to the physical aging and bacteriological attacks. In diverse countries the problem originated by the handling of non-biodegradable solid wastes fabricated with synthetic polymers derived from the petrochemical industry, is growing day with day. These solid wastes take about 150 years to degrade and reintegrate to the environment. Diverse research have been conducted to reduce the amount of plastic waste and to elaborate less aggressive products to the environment. Although the practice of recycle would seem a viable response for this problem, this is a limited solution, nevertheless not all the countries have the economic and technological infrastructure to its implementation. Thus, there is a great interest in the production of diverse biodegradable materials with similar functional characteristics that can replace the commercial plastics.

Some alternatives used for elaboration of “biodegradable plastics”, are the biopolymers (starch, proteins and others). These macro-molecules are biologically synthesized or fabricated by chemical processes from natural sources (Guilbert 1992), and can be modified by diverse processes. However most of these biopolymers individually processed showed poor mechanical properties and lack of dimensional stability resulting in very fragile products.

An alternative to diminish this problem is the incorporation of reinforcing materials within the matrix of the biopolymer like natural fibres. The amount and type of fibre added to the thermoplastic starch compositions will vary depending upon the desired properties of the final moulded article, with tensile strength, mechanical resistance, toughness, flexibility, dimensional stability and cost. Natural fibre is mainly formed of cellulose which is the most abundant natural polymer that has been investigated, with its derivatives, as potentially biodegradable raw materials. However, the natural cellulose, in case single, can not be processed easily to be used like biodegradable material, it can be used like reinforcement agent of other polymers, or by means of chemical modifications that alter their ordered

structure this can be used individually as it is the case of cellulose acetate (Armelin 2002), although any type of modification made to the raw materials involve additional costs.

Basically the technique used to manufacture synthetic plastics can be used for the manufacturing of biodegradable materials. The injection moulding may be performed using a known injection moulding machine, for example, an inline screw injection moulding machine, a multilayer injection moulding machine, or a double-headed injection moulding machine, according to an ordinary method; although using natural polymers requires a profound knowledge of these materials during their processing, related to the synthetic polymers. Thermoplastic extrusion and injection moulding are the most utilized technologies for the plastic manufacturing. Some researchers have reported that these processes can be utilized individually or together for the development of new thermoplastic products which can be used like biodegradable materials for the production of diverse degradable materials with similar or better characteristics than those of commercial plastics, although, with the advantage of decreasing the adverse effect of waste disposal on the global environment (Carr and Cunningham 1989).

The aim of this research was to evaluate the effect of the addition of fibre as a reinforcement material and glycerol in the production of moulded starch (plates as model), produced by the process of thermoplastic extrusion and injection moulding.

II. Raw Materials

a. Starch

Starch is one of the natural polymers that have been used as matrix for the production of reinforced biodegradable materials due to its characteristics of thermoplasticity, strong hydrophilicity, renewability, low cost and high availability (Cha and Chinnan 2004). The starch in its more stable conformation is a homopolymer of D-glucose. The monomers of D-glucose are bounded by linkages α -(1-4) (95% mainly) and by linkages α -(1-6). In fact, native starch is basically formed of two polymers with different primary structures: the amylose (20-30%), a linear molecule and the amylopectin (70-80%) a branched molecule. Some starches with high amylose or amylopectin content are commercially available. The molecules of amylose and amylopectin have masses that vary from 10^5 to 10^7 g/mol respectively (Whistler et al 1984).

Starch is a biopolymer of high availability in the nature, and it is extracted from diverse sources of cereals (corn, wheat, rice, and others), tubercles (potato, tapioca, and others), roots and in lesser proportion from some fruits and leguminous. The starch content in cereals vary from 30 to 80% in leguminous, from 25 to 50%, in tubercles, and from 60 to 90% in some fruits as banana with contents < 10% (dry base). The world-wide starch production in 2000 was 48.5 million tons that were extracted principally from corn, wheat and potato (Table 1).

Starch molecules have two important functional groups: -OH groups, susceptible to substitution reactions, and the C-O-C linkages susceptible to the breaking of the chains. The modification affecting these functional groups or the introduction of some chemical agents modify the structure of the chain, increasing viscosity, reducing the water retention and increasing the resistance to the mechanical effort of starch.

Table 1. Starch production by raw materials in 2000.

	Corn	Potato	Wheat	Others	Total
European Union	3.9	1.8	2.8	0.0	8.4
USA	24.6	0.0	0.3	0.0	24.9
Other countries	10.9	0.8	1.1	2.5	15.2
World	39.4	2.6	4.1	2.5	48.5

(Million tons) Source: European Commission (2002).

b. Fibre

Fibres may be added to the mouldable mixture to increase the flexibility, ductility, bendability, cohesion, elongation ability, deflection ability, toughness, and fracture energy, as well as the flexural and tensile strengths of the resulting articles. Fibres are unidimensional, long and thin structures which principal function is the tissue formation. The useful polymers as fibres are those that have a high degree of crystallinity and strong interaction between adjacent chains; this orientation increases the tensile force (Billmeyer 1984). Fibres have a high length to width ratio (or "aspect ratio") and are oriented throughout a single axis. They have great molecular cohesion, which makes them stronger than plastics, and for this reason they are used as reinforcement materials. Glass transition temperature and melting point are two important properties of fibres; a glass transition temperature (T_g) too high makes difficult the stretching, and therefore, the orientation of the fibre, and if the T_g is too low, the orientation of the fibre is not maintained at room temperature.

A wide range of fibres can optionally be used in order to improve the physical properties of the thermoplastic starch compositions because they readily decompose under normal conditions. In México natural fibre and co-products from agroindustrial processes include in many cases fibres extremely inexpensive and abundant such as cellulosic fibres extracted from wood, plant leaves, and plant stems, wheat pericarp, corn, sorghum, bagasse, sisal, palm, diverse agaves, coconut, and pineapple husk. However, some fibres may be preferred depending on the intended use and performance criteria of the article. In Mexico approximately 77 million of tons of agricultural residues are generated, 50% from corn, followed by wheat, sorghum and sugar cane (Muñoz 2002). Annually, about 11 million tons (dry basis) of bagasse are available; it represents a potential source of natural fibre. The availability of fibre residues generated in industrial applications can represent until 10% of the weight plant and plant stems, (Muñoz 2002).

III. Experimental Development

A. Sample Preparation

Native corn starch (Cremena) was purchased from IMSA (Mexico, D.F.). Bagasse was donated by regional farmers from Veracruz State. The natural fibres were previously sun dried and milled using a hammer mill (Pulvex, México D. F.) with a mesh of 4 mm, then the fibres were sifted to separate the impurities of the material collected. The fibres with a

diameter greater than 420 μm were used for the elaboration of the thermoplastic formulations. Glycerol (JT Baker, México D.F) was used as plasticizer agent, and was added to the formulations after milling and cleaning the fibre.

The analysed variables were glycerol content (0-20%) and fibre content (0-20%) in blends with starch. The blends were extruded with the objective to obtain pellets using a single screw extruder in a first step. Later the starch-fibre-glycerol partially plasticized in pellets; were dried and moulded. All the evaluated materials were processed in the same conditions; the materials were moulded using a plate form as system model (Figure 1), keeping constant the mould temperature.



Figure 1. Extruded and injected-moulded plate fabricated with starch reinforced with fibre.

B. Sample Characterization

Physicochemical, structural, mechanical and biodegradation analysis were performed in plates.

1. Physicochemical Analysis

a. Water Solubility Index (WSI)

WSI was determined according to the procedure described by Anderson et al (1969).

b. Colour

A tristimulus colorimeter (Hunter Lab) was used to register the luminosity values [luminosity, from 0 (black) to 100 (white)].

2. Structural Analysis

a. Infrared Spectroscopy Analysis (IR)

The IR patterns were registered using a spectroscopy Nicoler Avatar 360 FT-IR, following the methodology of Sandler et al (1998).

b. X-ray Analysis

The samples were evaluated using an X-ray diffractometer (Siemens D500) according to the procedure described by Zazueta-Morales (2002)

c. *Viscosity Profiles*

The viscosity characteristics were evaluated using equipment "Rapid Visco-Analyzer" (RVA), model 3C (Newport Scientific PTY Ltd., Sydney, Australia).

d. *Scanning Electronic Microscopy (SEM)*

The analyses of SEM were performed using an electronic microscopy Philips® Model XL30, using a secondary electron detector and a field of 15 (Cárabez-Trejo et al 1989).

3. Mechanical Analysis

The DMA analysis was carried out using an analyzer Rheometrics TA using the methodology of flexion in three points, with a frequency of 1 Hertz. The dimensions of the test samples were 10 X 25 mm and 4 mm thickness. The value of elasticity modulus (*E*) was determined at 30°C.

4. Biodegradation Analysis

The kinetic degradation was analyzed following the velocity of production of CO₂ according to the methodology reported by Gracida et al (2004), using the following species of fungi: *trichoderma virens* (ATCC 9645), *Penicillium funiculosum* (ATCC 11797), *Chaetomium globosum* (ATCC 6205), *Aspergillus niger* (ATCC 9642) and *Aureobasidium pullulans* (ATCC 15233).

IV. Results and Discussion

A. Physicochemical Analysis

1. Water Solubility Index (WSI)

Water solubility index (WSI) registered the capacity of disintegration of the biodegradable material when exposed to moisture. This property is of extreme importance in biodegradable material of packing in products that are transported or manipulated in zones of high humidity. When these products elaborated from starch absorb water usually take place a significant change in their mechanical properties (Guan and Hanna 2004). In all the studied area, an increase in fibre and a decrease in glycerol contents resulted in decreasing values of WSI of plates (Figure 2).

Also, an interaction between fibre and glycerol content was found. Increasing amounts of glycerol in the formulations have a lubricant effect during processing, decreasing the severity of the process and thus, maintaining the integrity of the starch granules, to such degree that it prevented that they were opened and dissolved in water. In general an increase in the degree of starch gelatinization opens and fractures its granular structure, increasing the water solubility (Sagar and Merrill 1995).

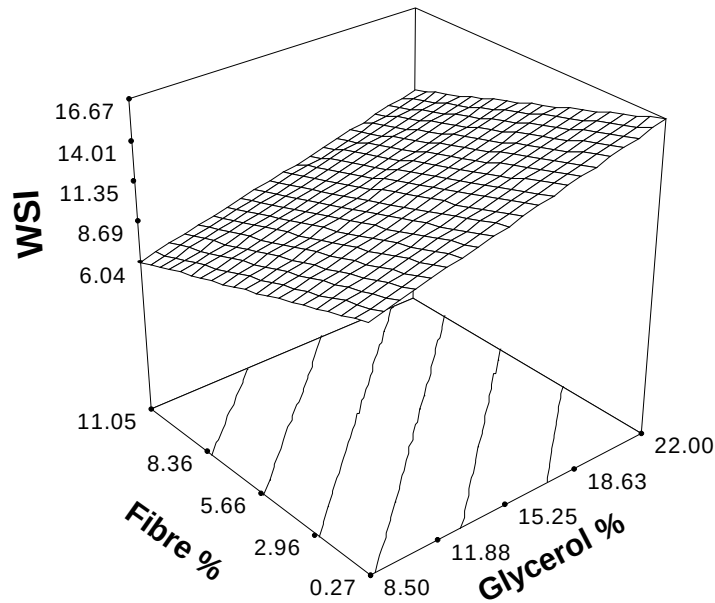


Figure 2. Effects of fibre and glycerol contents on WSI of biodegradable plates.

The insolubility of fibre affected the WSI values, resulting in high WSI values with increasing contents of fibre in the formulations. Although, some probable interactions could occur between starch-fibre-glycerol, which decreased the solubility of the material.

2. Colour

Extruded and injected-moulded biodegradable products elaborated with corn starch, fibre and glycerol, showed changes in the parameter of luminosity (L) due to an increase in the fibre content (Figure 3). This parameter showed a behaviour type chair and minimum values of L were found in plates with approximately 10% of fibre. These L values increased when either higher or lower fibre contents were used in the formulation.

At low fibre contents, an increase in the glycerol content increased the L values. However, high fibre contents with an increase in glycerol decreased these values. Low fibre contents darkened the plates probably due to the presence of residues of sugars and lignin from fibre. By other hand, increasing fibre contents resulted in decoloured materials, probably due to the increasing severity of the process that degrade the lignin and/or slightly darkened sugars and/or starch by effect of mechanical hydrolysis.

Diverse reactions like Millard, caramelization, hydrolysis, pyrolysis, oxidation, and pigment degradation could take place during extrusion and injection moulding processes, which could affect the colour of the final materials. The used extrusion conditions are known for favouring hydrolysis, caramelization and oxidation reactions of starch and sugars, which could lead to the formation of coloured or discoloured compounds (Camire et al 1990, Badui-Dergal 1993).

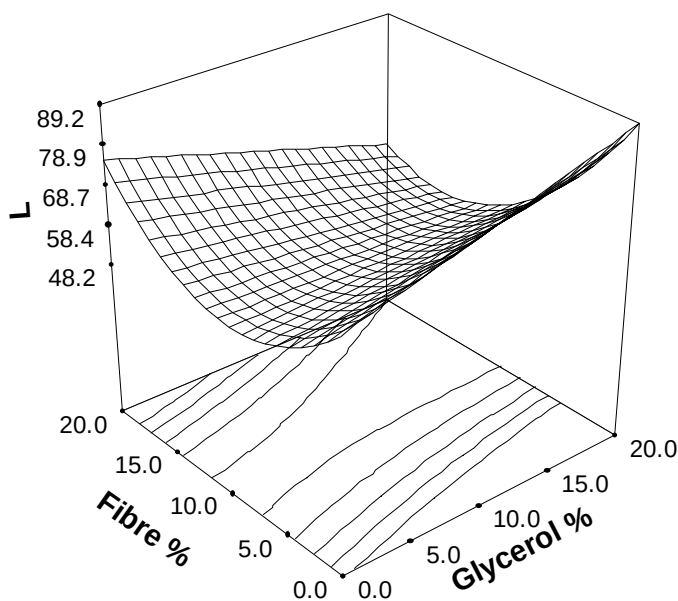


Figure 3. Effects of fibre and glycerol contents in colour (*L* parameter) of biodegradable plates.

B. Structural Analysis

Breaking and/or formation of new linkages or compounds during the processing of biodegradable polymers could modify the final structure of the materials.

1. Infrared Spectroscopy Analysis

The detection of functional groups is the main application of this technique. Figure 4 shows the different infrared patterns of the raw materials and the effects of glycerol and fibre contents in IR analysis. Fibre and starch showed peaks from 800 to 1200 cm^{-1} corresponding to the vibration modes of the C-C, C-O linkages and a mixture of the vibration modes of C-H linkages, solely with an evident difference due to the presence of a doublet from 1600 to 1700 cm^{-1} attributable to C=C linkages of the fibre. Similar results were reported by Mousia et al (2001) in the composition of nonexpanded biopolymer blends prepared by extrusion of mixtures of gelatin with either native or pregelatinized waxy maize starch.

The different types of vibrations of C-H linkages were localized in the area from 1900 to 3000 cm^{-1} (Dyer 1968). The reduction in the intensity of the peaks of vibration of C-H linkages found from 2800 cm^{-1} , probably can be attributed to the possible breaking of these linkages, due to the effect of the process. It was not registered an evident change in the infrared patterns by effect of the studied variables.

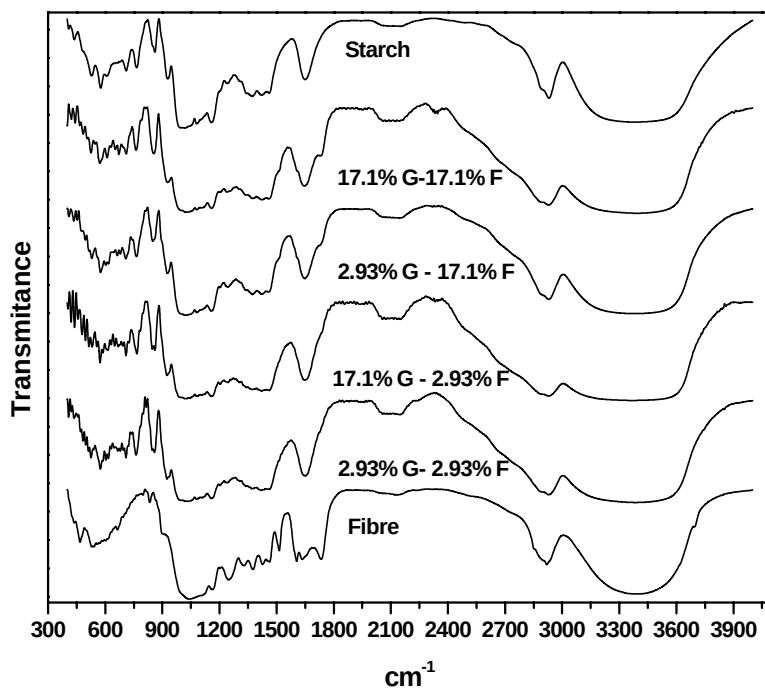


Figure 4. Effects of fibre and glycerol contents in infrared patterns of biodegradable plates.

2. X-ray Analysis

Most of the polymers have amorphous or almost completely amorphous diffraction patterns with the presence of some peaks and are known as semicrystalline polymers, as starch. The effect of the processing variables in the loss of the semicrystalline patterns indicates a plasticization of these materials. Figure 5 shows the effects of fibre and glycerol contents in X-Ray diffraction of moulded plates. Corn starch showed a diffraction pattern A type, characteristic of cereals, however, the fibre showed an almost amorphous pattern with the presence of a single peak at angle $2\theta \approx 20$. All the processed materials lost their native structure, and in most of them the patterns were completely amorphous, also, in some materials the formation of V_h patterns, typical of processed starches was registered.

The materials experimented almost complete plasticization during processing. Starch showed a similar structure than those of synthetic polymers, with high molecular weight and strong linkages between macro-molecules that facilitated the transformation to a thermoplastic material. The extrusion process destroyed completely the starch structure, leading to the formation of X-Ray patterns typical of an amorphous state and the formation of a new structure could be induced (Colonna et al 1989). Cairns et al (1997) reported that the presence of a V_h pattern of diffraction can be due to the formation of an amylose-lipid complex; this new structure is possible to be formed with lipid contents lower than 1% of starch.

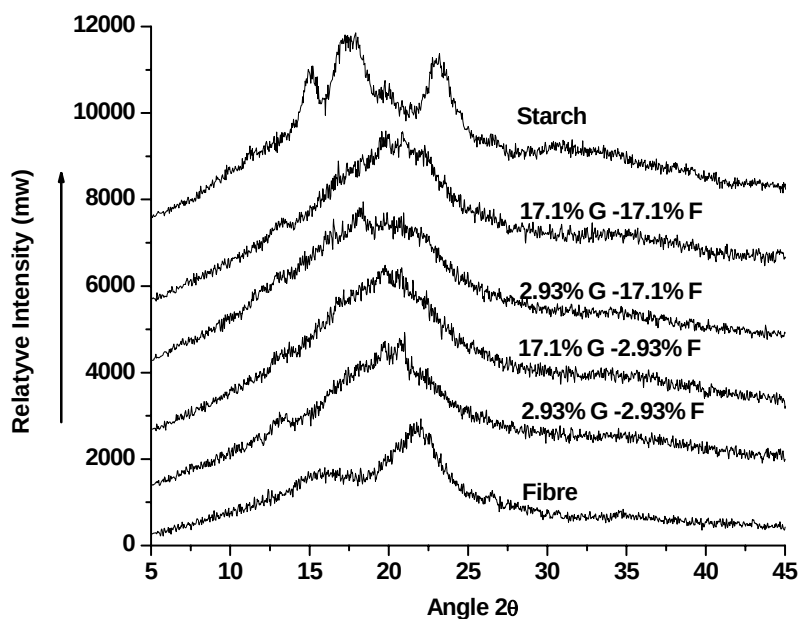


Figure 5. Effects of fibre and glycerol contents in X-ray diffraction of the biodegradable plates.

3. Viscosity Profiles

Figure 6 shows that the viscosity values were increased when the glycerol content was increased from 0 to 10%, attributable to the lubricant effect of the glycerol that decreased the severity of the process and, therefore, the degree of starch plasticization and the rigidity of the final materials. Yu et al (1998) reported that the severity of the process decreased the viscosity values. However, increasing the glycerol content from 10 to 20%, the viscosity values were decreased making possible an increase in the interactions starch-plasticizer, preventing the re-association of the starch chains which tend to form gels with the water (Zeng et al 1997). The addition of 10% of glycerol and increasing fibre content from 0 to 10% increased the values of viscosity, suggesting a possible reinforcing and a protective effect of the fibre on the starch. Although increasing the fibre content from 10 to 20% decreased the viscosity values.

According to Guam et al (2004), the components of the fibre, cellulose-hemicellulose-lignin are strongly bounded to each other, although they can be separated applying specific chemical treatments. The severe conditions of the moulding and extrusion processes probably induced the formation of some starch-fibre molecular linkages demonstrated by the increases in the viscosity values.

Probably in these conditions the glycerol penetrates the lignin-cellulose-hemicellulose matrix of the fibre and dissolves the linkages inducing the formation of new linkages between the fibre and starch, and also the loss of the structure by effect of glycerol. Therefore, greater fibre content in the formulations required high glycerol content in order to dissolve the matrix and to form new interactions between the components.

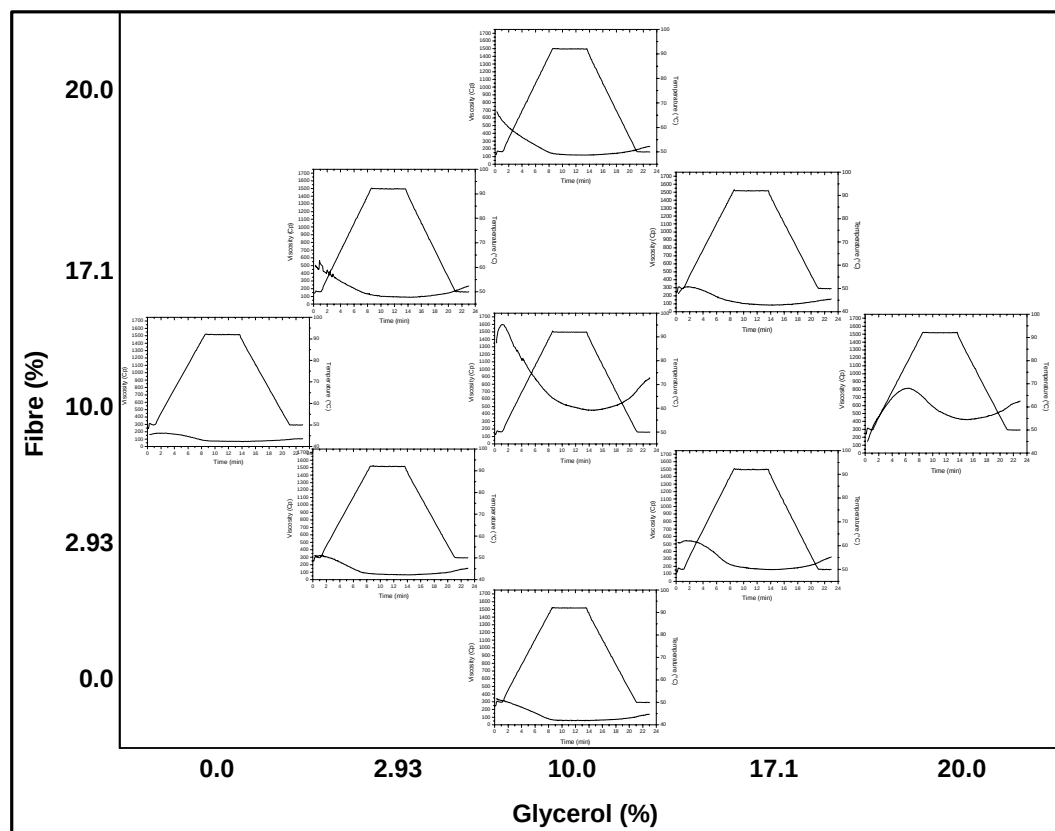


Figure 6. Effects of fibre and glycerol contents in viscosity profiles of biodegradable plates.

4. Electron Microscopical Analysis

Apparently the main changes that took place in the processed materials were fragmentation, gelatinization and plasticization of starch granules. Figures 7A and 7B show the microphotographs of raw fibre and native corn starch respectively.

The size of the fibre was heterogeneous. On the other hand, corn starch granules had a diameter size between 5 and 25 μ m, similar to the reported data by Alexander (1995). Also, Figures 7C and 7D show that during the preparation of pellets using the extrusion process, fragmentation of the granular structure and partial plasticization of the material took place; semi funded starch granules and a blend of the ingredients formed a matrix that entrapped the fibres. Thus, the extruded pellets showed a compact structure and a homogenous matrix between starch and fibre, with a partial plasticization of the blend with specific characteristics for its suitable posterior processing by injection moulding. The injection-moulding of extruded pellets was the most critical stage in the fabrication of biodegradable materials. Figures 7E and 7F show complete plasticization of the moulded materials. Specifically Figure 7E shows a cross section of a fibre fragment that was cut together with the plasticized starch matrix, suggesting a strong physical interaction between both materials, and resulting in a mechanical reinforcing of the extruded injected moulded materials. Figure 7F shows certain porosity in the surface of the injected material due to the evaporation of the deposited water. These interactions also were reported by Av  rous et al (2001), who indicated that a composite

elaborated from two natural polymers of cellulose and thermoplastic starch showed a better interaction than those of a composite elaborated from a synthetic source of low density polyethylene (LDPE) and natural fibre, resulting in a better effect of reinforcing which was reflected in its mechanical properties.

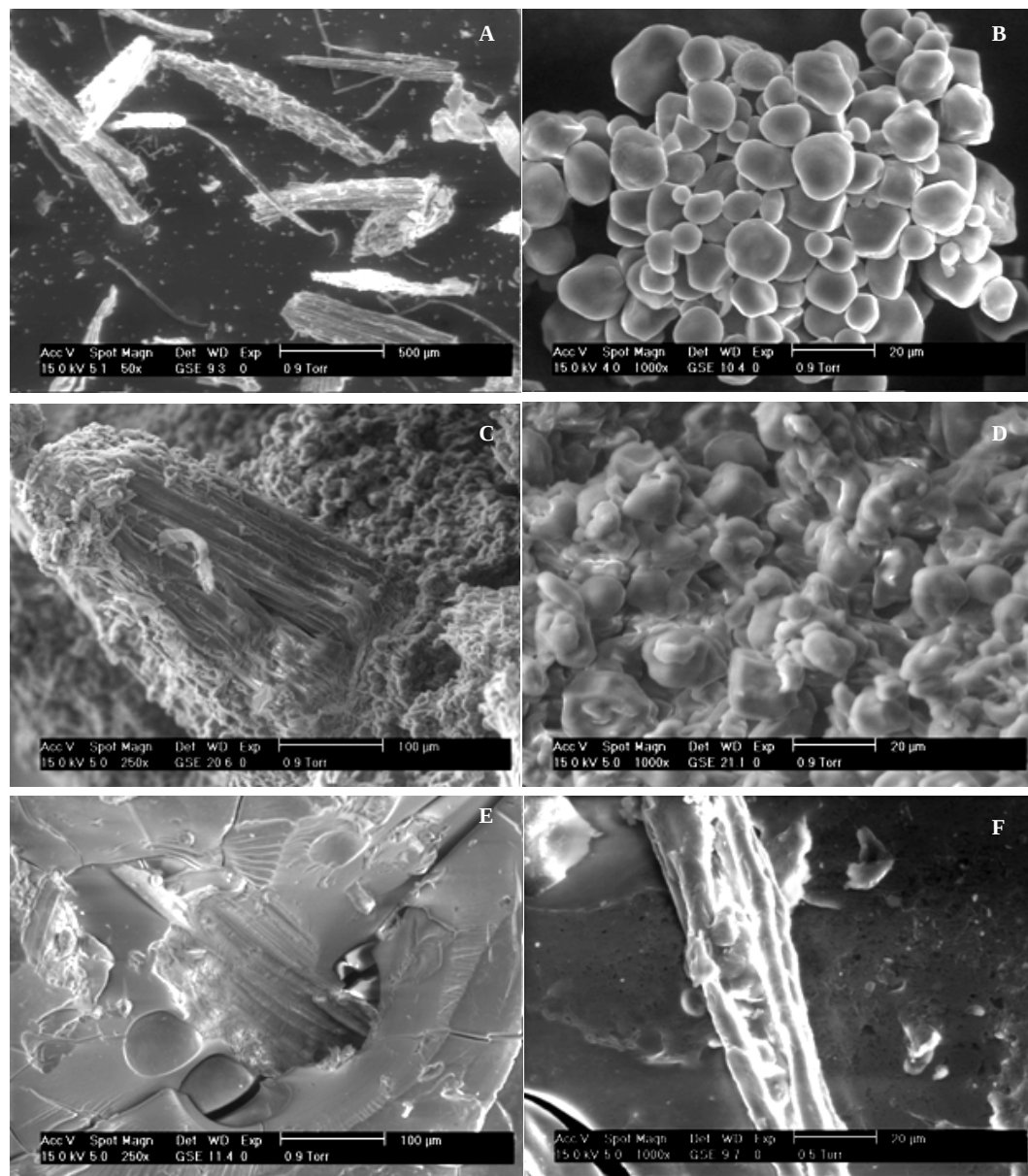


Figure 7. Microphotographs of the biodegradable materials in different stages of processing, A=Fibre, B=Corn starch, C and D= Extruded Pellets and E and F= Injected and moulded biodegradable plates.

C. Mechanical Analysis

The mechanical properties gave important information of the functionality of the biodegradable materials. Elasticity modulus (E), is a relation between the strength (σ) and the strain (ϵ) of a material; in general high values of E indicate that the material has high resistance to the deformation resulting in very rigid materials, as occur in plastic polymers. However, low values of E indicate that the material is easily deformed resulting in very smooth products, as take place in elastomers. In the present study an example of the changes in the values of E related to the fibre and glycerol contents in moulded starch products is showed in Figure 8. An increase in glycerol content from 0 to 20% significantly decreased the values of E from 1.38 to 0.71 GPa. By the other hand, an increase in the fibre content from 0 to 10% significantly increased the values of E from 0.75 to 1.19 GPa; in the same way an increase of fibre content from 10 to 20% showed an increase in the E values from 1.19 to 1.25 GPa, although this increase was not statistically significant. Similar values of E were reported by Mani and Bhattacharya (1998) in extruded and moulded blends of starches with different contents of amylose and ethylene-vinyl acetate.

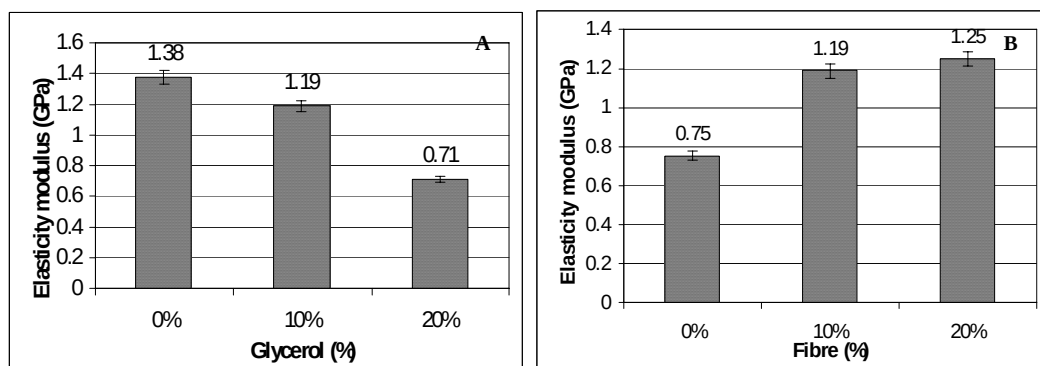


Figure 8. Effects of fibre (B) and glycerol (a) contents in changes of elasticity modulus of biodegradable plates.

An increase in the glycerol content conferred a plasticizing effect in the processed material avoiding the formation of interactions between starch molecules which are very rigid linkages, favouring by the other hand, the interactions starch-plasticizer-starch which are linkages that have greater mobility inducing the molecular displacement that resulted in more flexible and less rigid materials as the plasticizer content was increased, and thus, decreasing the values of E (Yu et al 1998).

The fibre content in the matrix of synthetic or biological polymers increased the values of elasticity modulus and maximum resistance to the tension; and decreased the values of elongation at fracture (Oskman et al 2003, Alvarez et al 2004, Brahmakumar et al 2005). Probably this effect is due to an interaction of the fibre with the matrix, decreasing the molecular mobility and resulting in more rigid and less flexible materials (Wu et al 2003).

D. Biodegradability Analysis

The biodegradability analysis indicated high velocity of production of CO₂ in all the materials after 7 days, in controlled conditions of analysis (Figure 9). The maximum production of CO₂ was for the sample with starch and glycerol followed for the sample with 10% of glycerol and 20% of fibre. The sample with 10% of glycerol and 10% of fibre showed the maximum CO₂ production after 11 days of exposition to the action of the microorganisms. Although the plates degrade over time in specific conditions, these articles possess a higher resistance to such degradation and will remain substantially intact for a more extended period of time when exposed to moisture, such as from the atmosphere, or from submersion in water or other direct contact with water.

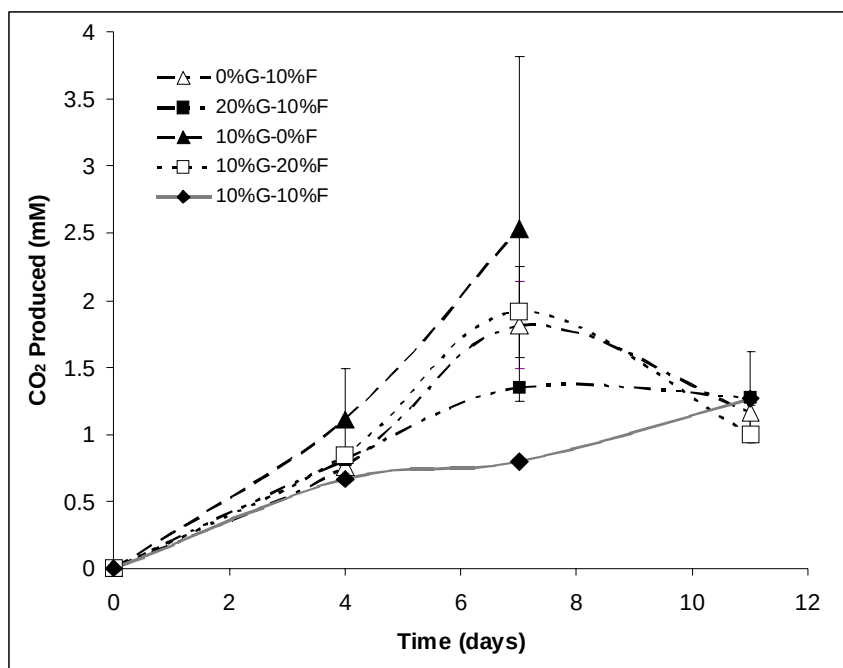


Figure 9. Effects of fibre and glycerol contents in biodegradability of biodegradable plates.

V. Conclusions

Thermoplastic formulations of starch blended with fibres improved the mechanical properties of biodegradable materials. The addition of glycerol to the formulations contributes to form a thermoplastic melt. The mechanical and structural properties of moulded plates were influenced by fibre and glycerol contents during the extrusion and moulding-injection processes. The spectroscopy IR indicated that there were no greater changes in the structure of the materials during the diverse stages of processing. The analysis of viscosity, DMA and microscopy, indicated the probable formation of interactions fibre -starch- plasticizer. Biodegradation analysis indicated that all the materials have a high speed of reintegration to the environment. The raw materials are available in great volumes, low cost and the overall

composition is environmentally friendly compared to conventional thermoplastic materials and offers the great potential to reduce the handling of the nonbiodegradable solids.

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Chapter 11

APPLICATION OF PHOSPHORYLATED WAXY MAIZE STARCH IN THE MICROENCAPSULATION OF FLAVORS: CHARACTERIZATION AND STABILITY

B. Murúa-Pagola¹, I. Beristain-Guevara² and F. Martínez-Bustos^{1*}

¹Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional-
Unidad Querétaro. Libramiento Norponiente No. 2000, Fracc. Real de Juriquilla,
Querétaro, Qro. MEXICO.

²Instituto de Ciencias Básicas, Universidad Veracruzana. Av. Dr. Luis Castelazo S/N Col.
Industrial Animas C.P. 91190. Xalapa, Veracruz km. 3.5. MEXICO.

Abstract

Commercial food flavors in liquid form are difficult to handle or incorporate into foods. Flavors are volatile and thus would readily evaporate from a food matrix during storage. Encapsulation provides a better retention of flavors and protection against light-induced reactions and oxidation. Various forms of modified starches are used for flavor encapsulation which includes emulsifying starches and starch hydrolysis products. The aim of this work was to prepare phosphorylated waxy maize starch by melting extrusion with sodium tripolyphosphate using a single-screw extruder, and its evaluation as shell material for encapsulation of orange peel oil using spray drying. Starches were hydrolyzed with hydrochloric acid before they were esterified (3.4% HCl, 6 h, 50°C). The viscosity of the modified starch was reduced as the hydrolysis products had smaller molecular weights than the native starch, while the water solubility index increased, making the modified starches appropriate for the encapsulation process using spray drying. Emulsions were prepared with 30% (w/w) of shell material and 20% of orange oil (w/w) by weight, based on the total weight of solids. The phosphorylated starch had a total oil retention of 55.7%. The addition of 2% (w/w) of whey protein concentrate (WPC) improved the emulsification process and oil retention to 66.8%. Encapsulated orange peel oil showed a good stability through 28 days of storage at room temperature and 50°C (50% HR) with an oil retention of 86% and 68% with respect of the starting oil in the capsules. The use of blends of starch-WPC improved the

* E-mail address: fmartinez@qro.cinvestav.mx. Telephone: (52) 442-4-41-49-05

emulsification process and oil retention during spray-drying. Phosphorylated starches are a good alternative of shell material of low cost for flavor encapsulation.

I. Introduction

Flavor plays an important role in consumer satisfaction and influences further consumption of foods. Flavor stability in different foods has been of increasing interest because of its relationship with the quality and acceptability of foods, but it is difficult to control. Manufacturing and storage processes, packaging materials and ingredients in foods often cause modification in overall flavor by reducing aroma compound intensity or producing off-flavor components (Lubbers et al 1998). Microcapsule formulations can achieve controlled, sustained or delayed release and protect oxygen sensitive core materials during processing and storage. Many flavors are volatile and can be retained in foods much more effectively when encapsulated (Brazel 1999). Encapsulation improves the food product overall. It can prolong shelf-life stability so that the nutritional value or flavor of foods does not diminish significantly between the dates of production and consumption.

1. Encapsulation

Encapsulation or microencapsulation is defined as a process by which one material or a mixture of materials is coated or entrapped within another material system. The particle size of most encapsulated flavor products is in the range of 0.2-5,000 μ (King 1995). The material that is coated or entrapped is most often a liquid but could be a solid particle or gas and is referred to by various names such as core material, payload, active, fill or internal phase. The material that forms the coating is referred to as the wall material, carrier, membrane, shell or coating. Encapsulation is used in a number of different industries with a wide variety of techniques or processes available (Risch 1995, Madene et al 2006). Flavor encapsulation is the general term for the various processes employed to deliver liquid flavors in a standardized, functional form. Flavors are indispensable ingredients of food preparations, but commercial food flavors in liquid form are difficult to handle or incorporate into foods. Moreover, many flavor components exhibit considerable sensitivity to oxygen, light, or heat, making necessary to protect them through encapsulation (Qi and Xu 1999). The benefits of encapsulating flavors are numerous: converting a liquid flavor into an easily dispensable powder, protecting a specific flavor or key flavor components from change, delivering more flavor impact in a finished product, supplying visually distinct, flavored particles, and in some instances, providing controlled-release functionality in a product application (Porzio 2004).

Encapsulation is typically carried out in commercial practice using one of a number of processes, including: spray-drying, spray-cooling/chilling, freeze-drying, fluidized-bed coating, extrusion, coacervation, co-crystallization, and molecular inclusion. A number of reviews of encapsulation have been published which include more details concerning particular techniques (Diezzak 1988, Shahidi and Han 1993, Risch 1995, Gibbs et al 1999, Thies 2001, Gouin 2004, Madene et al 2006).

Spray drying is the most common method of encapsulating food ingredients. It is still the most economical and widely used method of encapsulation, finding broad use in the flavor

industry. Equipment is readily available and production costs are lower than for most other methods of encapsulation (Risch 1995). The initial step in spray drying a flavor is the selection of a suitable carrier (or encapsulating agent). The ideal carrier should have good emulsifying properties, be a good film former, have low viscosity at high solids levels (<300 cps at >35% solids levels), exhibit low hygroscopicity, release the flavor when reconstituted in a finished food product, be low in cost, bland in taste, stable in supply, and afford good protection to the encapsulated flavor (Reineccius 2006). Hydrolyzed starches, modified starches and gum Arabic make up the three classes of carriers in wide use today (Reineccius 1991). Spray drying is divided into different steps: atomization, mixing of sprayed liquid and air, evaporation of water and separation of product. Before spray drying, one more step is necessary to transform feed liquid into powder: emulsification of flavors into small emulsion droplets within a carrier solution (O/W emulsion) by a homogenizer. Then the emulsion is fed into the spray dryer and transformed into droplets by an atomizer, followed by dehydrating in a hot air. Numerous studies have been conducted to evaluate the retention of flavor during spray drying and the shelf life of the spray-dried powder (Anandaraman and Reineccius 1986, Risch and Reineccius 1988, Westing et al 1988, Finney et al 2002, Beristain and Vernon-Carter 2002, Soottitantawat et al 2004, 2005).

1.1. Encapsulated Material (Orange Peel Oil)

The flavor industry depends heavily on true encapsulation techniques for rendering flavors into solids and offering them protection until consumption. Flavoring agents and spices are encapsulated by a variety of processes and offer numerous advantages to food processors. Flavor concentrates are oily and lipophilic materials. Microencapsulation has become an important approach to transform liquid food flavorings into stable and free-flowing powders that are easy to handle and to incorporate into a dry food system. Citrus fruits are a source of essential oils, which have a significant value as flavoring agents in several branches of food processing and soft drink manufacture. The worldwide popularity of citrus fruits is based largely on their nutritional value, flavor, aroma, and other intrinsic attributes such as texture and color. Their characteristic odor is due to essential oil in the peel, and the flavor of the juice is determined by the ratio of sugars to organic acids, mainly citric acid, overlaid by the presence of low levels of aromatics (Reineccius 2006).

Citrus oils are characterized by the presence of large percentages of monoterpenes (C_{10}/H_{16}) and smaller amounts of sesquiterpenes (C_{15}/H_{24}). Both are the carriers of the oxygenated compounds comprising alcohols (mostly linalool), aldehydes (largely octanal and decanal), ketones, acids and esters, which are responsible for the characteristic odor and flavor profiles (Reineccius 2006). Oxygenated components, especially the aldehydes, are the most important to the flavor of orange oil. Terpenes oxidize readily in the presence of air, leading to the development of undesirable flavors. To reduce this problem, concentrated orange oils are prepared by removing a portion of the terpenes. (Matthews and Braddock 1987). The composition of the various citrus oils is similar, the principle component being D-limonene (Reineccius 2006, Matthews and Braddock 1987). Limonene is a colourless liquid at room temperature with an extremely strong smell of oranges. It generates several oxidation products that are used to study the shelf life of encapsulated orange peel oil.

1.2. Encapsulation Matrices

Various carriers have been used to encapsulate flavors, including gums, starches and starch derivatives, sucrose, common salt, gelatin, waxes, fats, and proteins. Starch-based food ingredients used for flavor encapsulation include maltodextrins, corn syrup solids, cyclodextrins and emulsifying starches (OSA starches prepared with *n*-octenylsuccinic anhydride), or some combinations thereof (Shahidi and Han 1993, Reineccius 2006, Gibbs et al 1999, Qi and Xu 1999).

Because most of the active materials (especially the flavors) are insoluble in aqueous solutions and thus exist as emulsions, emulsion stability is viewed as a significant consideration for selection of a coating material. Maltodextrins and corn syrup solids have virtually no emulsion-stabilizing effect on water-insoluble components (Reineccius 1991). Also, maltodextrins and corn syrup solids do not result in good retention of volatile compounds during the spray-drying process (Shahidi and Han 1993). Hydrolyzed starches range in dextrose equivalent from about 2 to 36.5. They offer the advantages of being relatively inexpensive, bland in flavor, low in viscosity at high solids, and they may afford good protection against oxidation, depending on dextrose equivalent (Anandaraman and Reineccius 1986). Therefore, it is common to use blends of modified starches/hydrolyzed starches or gum Arabic/hydrolyzed starches (Reineccius 2006, Varavinit 2001, Kanakdande et al 2006, Bhandari et al 1992, McNamee et al 2001). Gum Arabic (acacia) is the traditional carrier used in spray drying. It is a good natural emulsifier, bland in flavor and provides good retention of volatiles during the drying process. Cost and limited supply of gum Arabic have led to the development of alternative carriers for spray drying.

Whey protein/carbohydrate mixtures have been used as wall solids in microencapsulation of anhydrous milkfat and volatiles (Young et al 1993, Sheu and Rosenberg 1995). In such systems, whey proteins functioned as emulsifying and film-forming agents while the carbohydrates (maltodextrins or corn syrup solids) were fillers and matrix-forming agents (Sheu and Rosenberg 1998).

1.2.1. Modified Starches

Starch granules are composed of two types of alphasuglucan, amylose and amylopectin, which represent approximately 98-99% of the dry weight. The ratio of the two polysaccharides varies according to the botanical origin of the starch. The waxy starches contain less than 15% amylose, normal starches 20-35% and high amylose starches greater than about 40% (Tester et al 2004). Amylose, with its long, straight chains, is known for forming strong, flexible films. Amylopectin, due to its branching, does not form as strong a film, but is noted for clarity and stability when forming gels and may show a slightly greater tendency towards absorption or binding of flavors. Starch, in its natural state, is cold water insoluble. When mixed with water and heated sufficiently to swell the granule, starch forms pastes which can produce strong films, but has viscosity too high for most encapsulation processes used in the food industry (Kenyon 1995).

Starch has been used as a food ingredient in a wide variety of products. However, native starch needs modification to develop desirable functional properties, such as solubility, texture, adhesion, dispersion, and heat tolerance (Kim et al 1999). Starch granules are insoluble in cold water and heat is required to achieve dispersion. Cooked native starch has a

high viscosity that is not desirable in certain applications (Landerito and Wang 2005). Chemically modified starches show markedly altered physicochemical properties as compared with the parent starches (Rutenberg and Solarek 1984).

Native starches and their hydrolysis products are hydrophilic in nature, thus having little affinity for hydrophobic flavor oils. Their hydrophilic nature can be changed by modifying them with *n*-octenylsuccinic anhydride (*n*-OSA). The modified starches contain hydrophobic octenyl side chains which impart an emulsifying capability to the starches (Qi and Xu 1999). With the incorporation of hydrophobic alkenyl groups into a normally hydrophilic starch molecule, the modified starch acquires surface active properties which are useful in stabilizing oil/water emulsions. Unlike typical surfactants, starch alkenyl succinates form strong films at the oil/water interface, giving the emulsion resistance to reagglomeration. As a result, aqueous solutions of starch alkenyl succinates and OSA starch, in particular, have been used to stabilize flavor concentrates in beverages, oil in salad dressings, and to encapsulate flavors, fragrances and vitamins in spray dried formulations (Shogren et al 2000). The Food and Drug Administration (FDA) has approved the treatment of starch with a maximum of 3% octenylsuccinic acid anhydride. This corresponds to a degree of substitution of 0.02. The modified starch obtained from this treatment has been reported to be superior to gum Arabic in emulsification properties and in the retention of volatile flavors during spray drying (Reineccius 2006).

Most *n*-OSA starches used for encapsulation are depolymerized to lower the viscosity in one of three ways: acid thinning or acid hydrolysis, pyrodextrinization and enzyme hydrolysis. These starches are widely used as encapsulating agents for spray drying and extruded flavors. However, *n*-OSA starch by itself does not normally provide satisfactory shelf life. Hence, starch hydrolysis products are generally used in combination with *n*-OSA starches to reduce the oxygen permeability of the matrix in spray-dried powders (Qi and Xu 1999).

Phosphorylation is another technique used to improve the functional properties of starch and to modify its behavior in terms of gelatinization, pasting, and retrogradation (San Martín-Martínez et al 2004). The introduction of negatively charged phosphate groups reduces interchain associations and facilitates starch hydration. Starch is usually phosphorylated by heating in the presence of chemicals such as sodium tripolyphosphate (STP) and sodium trimetaphosphate (SMP). The resultant starch phosphate gives a clear paste with increased solubility, swelling power, and freeze-thaw stability (Lim and Seib 1993, Solarek 1995). The conventional methods of starch modification require an excess amount of reagents and may cause environmental contamination from unreacted chemicals. Extrusion technology is a high-temperature, short-time process with the advantage of high versatility and absence of effluents (Harper 1981). Phosphorylation of starch by extrusion has progressed in recent years. During extrusion starch is heated, transported and compressed by the single screw or twin screws and pumped to a die at high temperature and pressure resulting in molecular changes. Extrusion cooking conditions can convert starch from a granular and semicrystalline material into a highly viscous, plastic material (Brümmer et al 2002). This conversion is accompanied by disruption of the crystalline structure of starch polymers and their reduction to smaller molecules (Vasanthan et al 2001).

Starch phosphates may be divided into two categories: starch phosphate monoesters in which a starch hydroxyl group is esterified with only one of the three acidic groups of phosphoric acid, and starch phosphate multiesters in which more than one of the acidic

groups of phosphoric acid are esterified. The latter is usually a mixture of mono-, di- and triesters of phosphoric acid. Depending on the degree of process modification, the modified starch may swell, disperse, or dissolve in cold water (Rutenberg and Solarek 1984). The FDA regulates the starch bound phosphorus according to the phosphorylating agent used. For starch modified with STP a limit of 0.4% has been set for phosphorus (Code of Federal Regulation 1991). Starch phosphates produced by extrusion has been reported for several food applications (San Martín-Martínez 2004, Salay and Ciacco 1990, Chang and Lii 1992, Seker et al 2003, Landerito and Wang 2005, Kim et al 1999), but there is no information about starch phosphates produced either by the oven heating process or by extrusion used for encapsulation purposes. The objective of this study was to prepare phosphorylated waxy maize starch by melting extrusion with sodium tripolyphosphate using a single-screw extruder, and its evaluation as shell material for encapsulation of orange peel oil using spray drying.

II. Raw Materials

Waxy maize starch (Corn Products, donated by CPI, Mexico) was used as a raw material for modification by the extrusion process with sodium tripolyphosphate (STP, Sigma-Aldrich), whey protein concentrate (WPC 80), purchased from IMSA, S.A. de C.V. (Mexico) and orange peel oil (Food Specialities, Mexico) as internal phase. A commercially modified Starch, N-LOK (National Starch and Chemical Co., donated by Arenal Mexico) was used as a control.

III. Methods

Starch Phosphorylation by Melting Extrusion

Starches were hydrolyzed with hydrochloric acid before they were esterified. Phosphorylation was performed using a laboratory single-screw extruder, designed and manufactured by Cinvestav-IPN, Mexico. Barrel temperatures were 70-80°C, 150°C and 180°C at the feeding, mixing and final extrusion sections respectively. Screw speed was 80 rpm and feed rate was 70 g/min, compression ratio screw of 3:1 and a 4.0 mm diameter die nozzle were used. Sodium tripolyphosphate (reagent grade, Sigma) was 4g/100g of starch. The moisture content of starch was 15-16% and pH was adjusted at 4.5-5.0. Samples were stored in polyethylene bags at 4°C for subsequent extrusion processing. Extruded blends were dried in a convection oven (40°C) for 2 h and milled using a hammer mill (model 200, Pulvex, Mexico) with a 250 µm sieve and packed in polyethylene bags for storage.

Spray Drying

Microencapsulation was performed by Spray Drying (Büchi Mini Spray Dryer Model 190, Laboratoriums Technik, AG, Flawil, Switzerland). Emulsions were prepared with 30% (w/w) of wall material and a proportion of 20% (w/w) of orange peel oil with respect to starch and

starch/WPC solids. The blends were homogenized with a Cole-Parmer high shear mixer (Cole Parmer Instrument Co., Chicago IL, U.S.A.) at 5,000 rpm for 5 minutes. Drying conditions were: inlet air temperature of 180°C and outlet air temperature of 110°C.

Physicochemical Characterization of Modified Starches

Water Solubility Index (WSI) and Water Absorption Index (WAI)

Both indexes were determined for the extruded starches following the method described by Anderson et al (1969). Three repetitions were made for each analysis.

Phosphorus Content

The phosphorus content in starch phosphates was determined by the method of Smith and Caruso (1964). Degree of substitution was calculated as follows:

$$DS = 162P/(3100-102P).$$

Where P = % phosphorus (dry basis) of the phosphorylated starch.

Viscosity Profiles

The pasting properties of starch phosphates were measured in a 3C Rapid Visco Analyzer (Newport Scientific PTY LTD, Sydney Australia). 2.5 g of sample were used. The measurements were made according to Zazueta et al (2002).

Microcapsules Characterization Total Oil Determination

The total oil in the microcapsules was determined using a Clevenger apparatus. 8 g of powder were dissolved in 150 mL of water in a 500 mL flask. The solution was distilled for 3 h. The volume of oil, read directly from the oil collection arm, was converted to grams of oil by multiplying by the density of the oil.

Surface Oil Determination

The amount of extractable surface oil on the dried powder was determined gravimetrically. The powder was extracted with hexane for 4 hr according to the method described by Beristain and Vernon-Carter (1994).

Scanning Electron Microscopy

The external morphology of the capsules was evaluated by scanning electronic microscopy (ESEM EDDAX, GSE detector), using an acceleration voltage of 20 kV. The encapsulated samples were fixed in stubs containing a double-faced adhesive metallic tape.

IV. Results and Discussion

Physicochemical Characterization of Modified Starches

Waxy maize starch was hydrolyzed before esterification in a preliminary study at the following conditions: 45°C, 9h, 4.5% HCl. The effects of acid concentration, temperature and hydrolysis time were studied in a previous work using an experimental design (data not shown), and the influence of independent variables on some physicochemical characteristics of phosphorylated starch were evaluated using response surface methodology (RSM). The optimal conditions of the hydrolysis stage were selected based on the water solubility index. Data analysis showed that only the temperature-acid concentration interaction was statistically significant ($P < 0.05$) from the studied factors, for this response. There were not significant differences between hydrolysis times, so the shorter time was selected. Solubility was higher at low acid concentration and high temperatures. Starch phosphates were hydrolyzed at 50°C, 3.4% HCl for 6h for the optimization process. Table 1 shows the WSI and WAI of phosphorylated starches. WPC was added to the starches before extrusion in concentrations of 2% and 5% (w/w). High solubility and low viscosity are desirable for a good encapsulating agent to be used in spray-drying. Results of preliminary study showed a similar solubility index for starch phosphates produced by extrusion, hydrolyzed at 45°C, 4.5% HCl for 9h. During acid thinning, the amorphous regions in the starch granules are preferentially hydrolyzed, though the granular structure is preserved (Qi and Xu 1999). Further dextrinization is required to obtain modified starches with good encapsulating characteristics. According to San Martín-Martínez et al (2004), high temperature and low water content lead to the highest values of WSI on starch phosphates produced by extrusion. The starch granule disintegrates completely or partially depending on the level of energy input, shearing effect, and pressure build-up during extrusion (Rubens and Heremans 2000). The severe extrusion conditions caused an extensive dextrinization of the starch, resulting in an increased formation of water-soluble products (Harper 1992).

Table 1. Water absorption index and water solubility index of starch phosphates prepared by melting extrusion

Sample ^a	WAI	WSI
Starch Phosphate	3.07	61.11
Starch Phosphate + 2% WPC	2.91	60.53
Starch Phosphate + 5% WPC	3.14	60.87
N-LOK	N.D.	91.00

^a Hydrolysis conditions (45°C, 9 h, 4.5% HCl). WPC was added to hydrolyzed starch before extrusion. N.D. Not determined. N-LOK: commercial starch was used as control

The phosphorus content of modified starches is showed in Table 2. Phosphorus content and degree of substitution of starch phosphates agree with those of Chang and Lii (1992). Kim et al (1999) found that the incorporation of phosphorus to rice starch was 0.376% using 4% of STP at 180°C. Reports in the literature on the effectiveness of STP in starch phosphorylation are inconsistent. Landerito and Wang (2005) produced starch phosphates with waxy maize starch with a phosphorus content of 1.6%. San Martín-Martínez et al (2004) reported a D.S. value of 0.018 when they used 4.18% of STP. The phosphorus content and degree of substitution of starch phosphates of this study were higher using the same amount of STP. The discrepancies as reported are most likely due to differences in extrusion conditions, sources of materials, and methods of analysis. The D.S. of starch phosphate + 5% of WPC was the lowest of the evaluated samples, probably due to an interaction between the starch and proteins.

Table 2. Phosphorus content of modified starches and degree of substitution

Sample	Phosphorus Content (%)	D.S. ($\times 10^{-2}$) ^a
Starch Phosphate	0.75	4.0
Starch Phosphate + 2% WPC	0.72	3.9
Starch Phosphate + 5% WPC	0.48	2.6
Starch Phosphate ^b	0.87	4.6

^a Degree of Substitution

^b Hydrolysis conditions (50°C, 3.4% HCl, 6h)

Figure 1 shows the viscosity profiles of waxy maize starch and modified starches phosphorylated by conventional method or by extrusion.

The starch phosphates modified by the extrusion process did not develop viscosity, as they were hydrolyzed before extrusion. Usually extrusion modified starches exhibit a lower viscosity profile compared with starches that have been modified by conventional processes. This can be attributed to disintegration of starch structure from the high shearing, pressure and temperature conditions during extrusion (Chang and Lii 1992). Starch phosphates modified by the conventional method were not hydrolyzed before modification and they exhibited a higher viscosity than unmodified starches. These results agree with those reported by Chang and Lii (1992).

The type of carrier used does influence flavor retention during spray drying. Some carrier materials become very viscous at relatively low solids contents. Low solids denote poor flavor retention. Carriers which are good emulsifiers and/or good film formers typically yield better flavor retention than do carriers which lack these properties (Reineccius 1988).

Microcapsules Characterization

Encapsulation performance of modified starches and the control (N-LOK) using spray drying is shown in Table 3. Starch phosphates were prepared using 2 and 5% of WPC during the extrusion process. Starch phosphate exhibited a total oil retention of 40.6% that was improved to 50.1% when the blend of 98:2 (w/w) of starch: WPC were phosphorylated by extrusion. The better results in terms of total oil retention (66.8%) were obtained when 2% of WPC was

added to the starch phosphate for emulsion preparation before spray drying. The flavor retention was higher for small amounts of WPC added to starch during extrusion or before spray-drying.

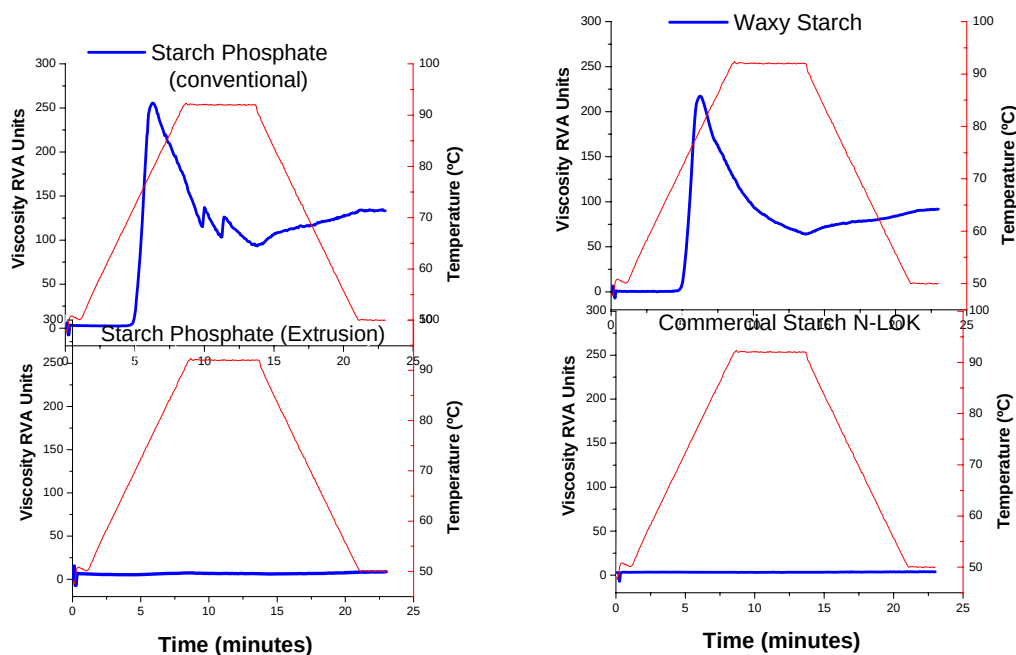


Figure 1. Viscosity profiles of starch phosphates

Table 3. Encapsulation performance of modified starches after spray drying

Sample	Starting Oil (g/100g)	Total Oil (g/100g)	Surface Oil (g/100g)	Total Oil Retention (% w/w)	Inner Oil Retention (% w/w)
Starch Phosphate ^a	20	8.1	0.38	40.6	95.2
Starch Phosphate + 2% WPC ^{a,b}	20	10.0	1.0	50.1	89.4
Starch Phosphate + 5% WPC ^{a,b}	20	7.8	0.9	39.0	88.4
Starch Phosphate + 2% WPC ^{a,c}	20	13.3	1.1	66.8	91.2
Starch Phosphate + 5% WPC ^{a,c}	20	10.0	0.7	50.1	92.8
Starch Phosphate ^d	20	11.2	0.7	55.7	93.0
N-LOK	20	17.8	0.7	89.1	95.6

a Hydrolysis conditions (45°C, 9 h, 4.5% HCl).

b WPC was added before the extrusion process

c WPC was added to the extruded starch before spray-drying.

d Optimized hydrolysis conditions (50°C, 6 h, 3.4% HCl).

N-LOK: commercial starch was used as control

The use of whey protein and carbohydrate wall systems have been reported by Sheu and Rosenberg (1995) as effective for volatile microencapsulation by spray drying using different ratios of WPI:carbohydrates. Young et al (1993) used mixtures of whey proteins with natural or modified carbohydrates for microencapsulation of anhydrous milkfat. In such systems, whey proteins served as emulsifying and film-forming materials (Sheu and Rosenberg 1995). In the present work, WPC was used in a very little proportion to improve the emulsifying properties of starch phosphates. Starch phosphates are considered to be good emulsion stabilizers (Solarek 1989) rather than true emulsifiers. The retention of orange peel oil during spray drying was influenced by the emulsifying properties of the shell materials, the proportion of starch:WPC and the stage of the process where WPC was added. Starch phosphates hydrolyzed under the optimized conditions improved total oil retention during spray drying to 55.7%.

The stability of the internal phase during storage was studied at room temperature and at 50°C (50% H.R.). Soottitantawat et al (2004) reported that at this condition the highest release and oxidation rate were observed without the change of external structure of the particles. Starch phosphate was used as shell material individually to study the release of flavor from the spray-dried powder at constant humidity and temperature. The internal phase exhibited good shelf life stability. At room temperature, the starch phosphate retained 86% of the encapsulated material; at 50°C there was an oil reduction up to 68%. The results of this study indicated that the differences in shelf life were accentuated at higher temperatures (data not shown).

Figure 2 shows microphotographs of microcapsules of starch phosphates and control.

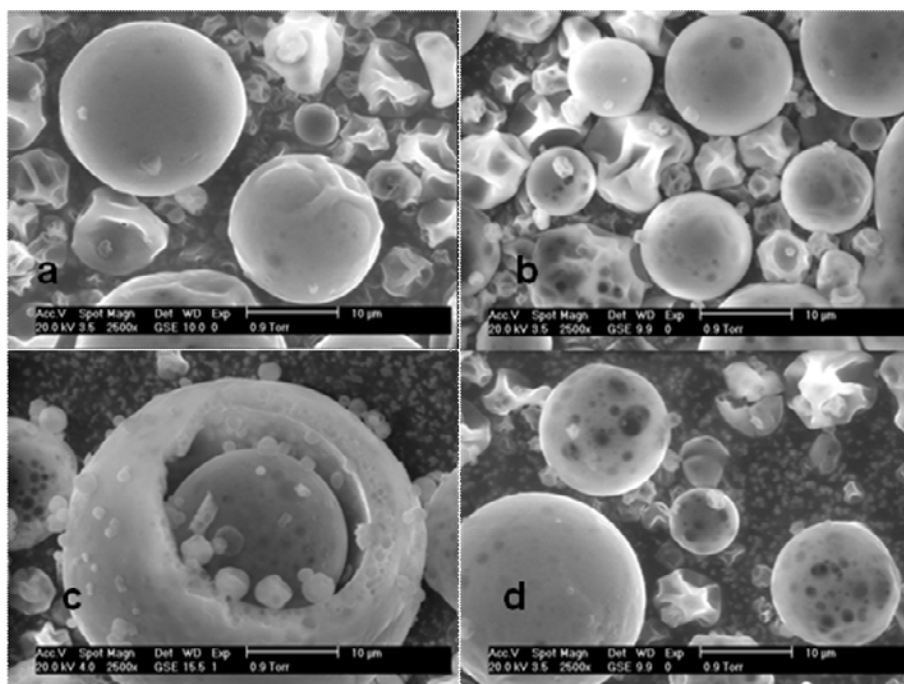


Figure 2. Physical structure of encapsulated orange oil powder. Wall materials: (a) Starch Phosphate, (b) Starch Phosphate + 2% WPC during extrusion, (c) N-LOK (d) Starch-phosphate + 2% WPC before spray-drying.

The external structure of the encapsulated powder was observed by SEM. One reason for using SEM in the research of microencapsulation is the need to determine the encapsulating ability of different polymers. Indication of this ability is given by the degree of integrity and porosity of the microcapsules (Rosenberg et al 1985). Capsules obtained with N-LOK and starch phosphate showed similar external morphologies with a rounded external surface. No pores or cracks were observed.

The inner structure of N-LOK capsules are shown in Figure 2c. The image shows how the core material is organized within the dried matrix. The inner structure of the open capsule was found without any deliberate fracturing. In the center there is a void which occupies most of the capsule volume. The core material was dispersed in the wall of the capsule in the form of small droplets.

V. Conclusions

Starch phosphates were produced by melting extrusion for encapsulation purposes. Blends of starch phosphate:WPC showed better total oil retention than starch phosphates individually. Starch phosphates provided a good protection of encapsulated orange peel oil during the shelf life study. The negatively charged groups introduced to starch phosphate improved the emulsifying capabilities of the starch making it a good alternative for the encapsulation of flavors. The extrusion process enhanced the fragmentation of starch producing a shell material with better characteristics of solubility and viscosity.

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Chapter 12

A FORECAST ANALYSIS ON FOOD NUTRITION SUPPLY AND DEMAND WORLDWIDE

***Wenjun Zhang^{1*}, Wengang Zhou^{1*},
Xiyan Zhang^{2*} and Yongkai Xia²***

¹Research Institute of Entomology, School of Life Sciences, Sun Yat-sen (Zhongshan)
University, Guangzhou 510275, China.

²Lucheng Banana Institute of Hainan, Hainan 570216, China

Abstract

This paper aimed to make a longer-term forecast analysis on global food nutrition supply and demand. The forecasts of supplies of food calories and proteins for the world and various regions over the period 2010-2030 were given, and food nutrition supply and demand balance in the forecast period was discussed.

If the past pattern continues, the global total food calorie supply would grow at the annual rate of 13.43 ± 0.71 kcal/cap/day and reach 3210.4 ± 67.3 kcal/cap/day in 2030. Total food calorie supplies for all of the regions would grow during the forecast period and, in most regions they are forecast to be greater than 3000 kcal/cap/day from 2015-2020. Total food protein supply for all regions but not Oceania, is forecast to grow during the forecast period. The proportion of animal sourced protein in total food protein supply is in 2030 forecast to increase and reach 35.5%, 61.6%, 56.8%, and 21.7% for Asia, Europe, South America, and Africa.

Food calorie supply in the world is expected to exceed the adequate energy intake after around 2015. Strong focus should be worldwide put on the over-intake of food calorie in the near future. Global food protein supply is not expected to be greater than the adequate range during the period 2010-2030. Food protein supply in Africa and Caribbean would be just a little greater than the basic demand in the forecast period. Food protein intake in these regions should be improved in the coming years.

Key Words: Food; Calories and protein; Supply and demand; Forecast; World

* E-mail address: zhwj@mail.sysu.edu.cn

* E-mail address: zhwgang_306@163.com

* E-mail address: zxyan1981@163.com

1. Introduction

There are 0.85 billion of chronically or acutely malnourished people in the world, mostly in Asia and Africa¹. More than 90% of them are chronically malnourished and 10% are acute hunger. Hidden hunger from micronutrient deficiencies additionally affects more than 2 billion people worldwide¹. Moreover, the numbers of malnourished people are increasing². Increased population and rapid urbanization will drive sustained growth in food demand³. The demand for higher valued commodities, such as meats and vegetables is also increasing⁴. According to a baseline projection, global cereal production was estimated to increase by 56% between 1997 and 2050, and livestock production by 90%. Developing countries will account for 93% of cereal demand growth and 85% of meat-demand growth to 2050^{4,5}. By 2020, world demand for rice, wheat, and maize is projected to increase by ~40% and livestock production by more than 60%⁶. By 2050, global population was projected to be 50% larger than at present and global grain demand is projected to double. This doubling will result from a projected 2.4-fold increase in per capita real income and from dietary shifts towards a higher proportion of meat⁷.

Given the pace of global change, human welfare is utterly dependent upon forward-looking, adaptive, and informed decisions⁸. Translation of data into a workable set of social indicators will enable policy debate to be conducted in an illuminating manner⁹. Meanwhile, having these research data available to assess rapidly emerging problems and quickly respond to public outcries for a solution would offer significant benefits to publics¹⁰. Since the era of Malthus, forecasts of food security have been an important part of the policy decision-making. Over the past decades, some researchers have expressed concern about the ability of food supply to keep up with food demands, whereas others have forecast that modern technologies or expansions of cultivated area would boost production sufficiently to meet rising demands¹¹⁻¹⁴. Food production must be coupled with both poverty reduction and environmental conservation, which makes the balanced food supply-demand even more difficult^{3,15}. As a consequence, the forecast and outlook of food supply and demand based on the latest data is therefore necessary for having an in-depth insight into these questions. On the other hand, regional problems in food distribution can be difficult to counter even when global supplies are adequate. To ask merely whether global food supplies can be sustainably increased to meet future requirements misses much of the question⁹. Regional forecasts would thus be more informative compared to merely global forecast. A number of agricultural businesses would also benefit from the ability to forecast food supply at regional scale¹⁶.

This paper tried to make a longer-term forecast analysis on global food nutrition supply and demand, and provide researchers with basic data on food nutrition supply and demand in the future. The forecasts of food nutrition supplies for the world and various regions over the period 2010-2030 were conducted. Balance of food nutrition supply and demand in the forecast period was discussed.

2. Materials and Methods

2.1. Data Source

Belonging to a poverty solution-oriented topic and due to the data availability, food nutrition in present study means only calories and protein provided by food products. Annual data on daily per capita supplies of food calories and proteins from animal and vegetable products since 1961 for the world, the developed countries, the developing countries, Africa, Asia, Caribbean, Europe, North & Central America, South America, and Oceania were obtained from the recent records of UN Food and Agriculture Organization¹⁷. Detailed definition of developed and developing countries can be found in the publications of FAO before 2006.

2.2. Forecast Model

Mechanistic forecasting of agriculture and social development is difficult and imprecise. In this study I fitted the dynamics of food nutrition supplies with the polynomial function: $x(t)=c+b_1 t+ b_2 t^2+ b_3 t^3+\dots$, where t is year. It was found that the dynamics of food nutrition supplies for various regions could be optimally fitted by the first-order polynomial function. We thus used the following univariate general linear model (GLM)^{18,19} to fit the dynamics of food nutrition supplies: $x(t)=c+r t$, where t is year, $x(t)$ is food nutrition supply at the year t , and r is the annual rate of food nutrition supply. The model was statistically tested with F -test against the adjusted R^2 of the GLM.

All forecasts and their confidence intervals were calculated from GLM. These forecasts were made over the period 2010-2030. They were model extrapolations of past trajectories and thus assumed similar technological and social patterns in the forecast period. In addition, the forecast based on mechanistic model with various variables could supplement our forecasts and are thus needed.

3. Results

Overall the GLM showed a better fitness on trajectories of food nutrition supplies in most cases (Table 1), so it may be used to represent the longer-term trends of global food nutrition supplies. Detailed forecasts of global food nutrition supplies, over the period 2010-2030, are given in Table 1. In order to analyze variability and similarity across regions and periods, we will compare the changes in the year 2030 relative to the current values. Current supplies were extrapolated from the GLM²⁰.

Table 1. GLM forecasts of global supplies of food calorie and protein over the period 2010 to 2030. r : the annual rate of food calorie or protein supply, $\geq r$: half-width of the confidence interval for r ($p < 0.05$), $x(t)$: the forecast, $\geq x(t)$: half-width of the confidence interval for $x(t)$ ($p < 0.05$), Adj R^2 : adjusted R^2 . Significance levels for GLM: **: $p < 0.01$, *: $p < 0.05$.

			World	Africa	Asia	Caribbean	Developed Countries	Developing Countries	Europe	N & C America	Oceania	South America
Total Food Calorie Supply	(kcal/cap/day/yr)	r	13.427	8.2067	20.696	7.1121	6.5216	18.824	4.4964	18.417	1.2838	12.486
		$\geq r$	0.706	0.458	1.144	3.458	1.304	0.918	1.938	0.592	1.117	0.927
		Adj. R^2	0.972**	0.969**	0.969**	0.279**	0.706**	0.976**	0.333**	0.989**	0.095	0.946**
	Food Calorie (kcal/cap/day)	2010 $x(t)$	2941.8	2492.8	2919.3	2600.0	3372.6	2865.0	3379.7	3595.4	2995.6	2941.6
		2010 $\geq x(t)$	61.4	39.8	99.5	300.7	113.3	79.9	168.6	51.5	97.1	80.6
		2015 $x(t)$	3009.0	2533.8	3022.8	2635.5	3405.2	2959.1	3402.2	3687.4	3002.0	3004.0
		2015 $\geq x(t)$	62.6	40.6	101.5	306.7	115.6	81.5	171.9	52.5	99.0	82.2
		2020 $x(t)$	3076.1	2574.8	3126.2	2671.1	3437.8	3053.2	3424.7	3779.5	3008.4	3066.4
		2020 $\geq x(t)$	64.0	41.5	103.7	313.5	118.2	83.3	175.8	53.7	101.2	84.1
		2025 $x(t)$	3143.2	2615.9	3229.7	2706.7	3470.4	3147.3	3447.2	3871.6	3014.8	3128.8
		2025 $\geq x(t)$	65.6	42.6	106.3	321.2	121.1	85.3	180.1	55.0	103.7	86.1
		2030 $x(t)$	3210.4	2656.9	3333.2	2742.2	3503.0	3241.4	3469.6	3963.7	3021.2	3191.3
		2030 $\geq x(t)$	67.3	43.7	109.0	329.5	124.2	87.5	184.7	56.4	106.4	88.4
Animal Calorie Supply	(kcal/cap/day/yr)	r	2.9378	0.302	6.614	-1.5065	1.7218	5.4946	1.5254	-0.0844	-6.0874	5.101
		$\geq r$	0.191	0.213	0.578	1.438	1.014	0.458	1.707	0.531	0.753	0.676
		Adj. R^2	0.958**	0.146**	0.927**	0.077*	0.204**	0.933**	0.051	0	0.863**	0.846**
	Food Calorie (kcal/cap/day)	2010 $x(t)$	479.9	182.6	406.1	345.3	922.1	380.6	1000.8	806.5	811.8	621.9
		2010 $\geq x(t)$	16.7	18.5	50.2	125.0	88.2	39.9	148.4	46.1	65.5	58.8
		2015 $x(t)$	494.6	184.2	439.2	337.7	930.7	408.1	1008.5	806.1	781.3	647.4
		2015 $\geq x(t)$	17.0	18.9	51.2	127.5	89.9	40.7	151.4	47.0	66.8	60.0
		2020 $x(t)$	509.2	185.7	472.2	330.2	939.3	435.6	1016.1	805.7	750.9	672.9
		2020 $\geq x(t)$	17.4	19.3	52.4	130.3	91.9	41.6	154.7	48.1	68.3	61.3
		2025 $x(t)$	523.9	187.2	505.3	322.7	947.9	463.1	1023.7	805.3	720.4	698.4
		2025 $\geq x(t)$	17.8	19.8	53.6	133.5	94.2	42.6	158.5	49.2	69.9	62.8
		2030 $x(t)$	538.6	188.7	538.4	315.1	956.5	490.5	1031.4	804.8	690.0	723.9
		2030 $\geq x(t)$	18.3	20.3	55.0	137.0	96.6	43.7	162.6	50.5	71.7	64.5

Table 1. Continued

			World	Africa	Asia	Caribbean	Developed Countries	Developing Countries	Europe	N & C America	Oceania	South America
Vegetable Calorie Supply	(kcal/cap/day/yr)	r	10.489	7.9047	14.082	8.6185	4.7998	13.33	2.971	18.502	7.3712	7.3848
		$\geq r$	0.77	0.4623	1.3509	2.3165	0.5702	1.1063	0.7579	0.5495	0.7018	0.8052
		Adj. R^2	0.947**	0.966**	0.913**	0.569**	0.873**	0.934**	0.595**	0.991**	0.915**	0.891**
	Food Calorie (kcal/cap/day)	2010 $x(t)$	2461.9	2310.1	2513.2	2254.7	2450.5	2484.3	2378.9	2788.8	2183.8	2319.7
		2010 $\geq x(t)$	67.0	40.2	117.4	201.4	49.6	96.2	65.9	47.8	61.0	70.0
		2015 $x(t)$	2514.4	2349.6	2583.6	2297.8	2474.5	2551.0	2393.7	2881.3	2220.7	2356.6
		2015 $\geq x(t)$	68.3	41.0	119.8	205.4	50.6	98.1	67.2	48.8	62.2	71.4
		2020 $x(t)$	2566.8	2389.2	2654.0	2340.9	2498.5	2617.6	2408.6	2973.8	2257.5	2393.5
		2020 $\geq x(t)$	69.9	41.9	122.4	210.0	51.7	100.3	68.7	49.9	63.6	73.0
		2025 $x(t)$	2619.3	2428.7	2724.4	2384.0	2522.5	2684.3	2423.4	3066.4	2294.4	2430.5
		2025 $\geq x(t)$	71.6	42.9	125.4	215.1	53.0	102.8	70.4	51.1	65.1	74.8
		2030 $x(t)$	2671.7	2468.2	2794.8	2427.1	2546.5	2750.9	2438.3	3158.9	2331.2	2467.4
		2030 $\geq x(t)$	73.4	44.1	128.7	220.7	54.4	105.4	72.2	52.4	66.8	76.7
Total Food Protein Supply	(g protein/cap/day/yr)	r	0.3294	0.15494	0.56962	0.13591	0.22742	0.49773	0.26185	0.36651	-0.07128	0.34416
		$\geq r$	0.019	0.018	0.038	0.101	0.053	0.035	0.072	0.033	0.063	0.056
		Adj. R^2	0.967**	0.883**	0.956**	0.133**	0.633**	0.952**	0.556**	0.926**	0.092*	0.783**
	Food Protein (g protein/cap/day)	2010 $x(t)$	77.87	61.66	74.69	60.95	103.74	72.29	104.12	102.84	95.42	76.92
		2010 $\geq x(t)$	1.66	1.52	3.29	8.74	4.66	3.04	6.28	2.80	5.46	4.89
		2015 $x(t)$	79.52	62.44	77.54	61.63	104.88	74.77	105.43	104.68	95.07	78.64
		2015 $\geq x(t)$	1.69	1.56	3.36	8.92	4.76	3.10	6.40	2.85	5.57	4.98
		2020 $x(t)$	81.16	63.21	80.39	62.30	106.01	77.26	106.74	106.51	94.71	80.36
		2020 $\geq x(t)$	1.73	1.59	3.44	9.12	4.86	3.17	6.55	2.92	5.70	5.10
		2025 $x(t)$	82.81	63.99	83.24	62.98	107.15	79.75	108.05	108.34	94.35	82.08
		2025 $\geq x(t)$	1.77	1.63	3.52	9.34	4.98	3.24	6.71	2.99	5.84	5.22
		2030 $x(t)$	84.46	64.76	86.09	63.66	108.29	82.24	109.36	110.17	94.00	83.80
		2030 $\geq x(t)$	1.82	1.67	3.61	9.58	5.11	3.33	6.88	3.07	5.99	5.36

Table 1. Continued

			World	Africa	Asia	Caribbean	Developed Countries	Developing Countries	Europe	N & C America	Oceania	South America
Animal Protein Supply	(g protein/cap/day/yr)	r	0.207	0.037	0.363	0.012	0.283	0.31	0.303	0.122	-0.081	0.349
		$\geq r$	0.010	0.014	0.035	0.064	0.065	0.031	0.091	0.025	0.064	0.041
		Adj. R^2	0.977**	0.401**	0.914**	0	0.65**	0.909**	0.513**	0.707**	0.115	0.873**
		2010 $x(t)$	29.75	13.30	23.28	22.95	61.47	22.18	61.29	57.57	60.71	40.63
		2010 $\geq x(t)$	0.87	1.21	3.01	5.57	5.58	2.66	7.90	2.13	5.61	3.62
		2015 $x(t)$	30.78	13.49	25.10	23.01	62.88	23.73	62.81	58.18	60.30	42.38
		2015 $\geq x(t)$	0.88	1.24	3.07	5.68	5.69	2.72	8.06	2.17	5.73	3.69
		2020 $x(t)$	31.81	13.67	26.91	23.07	64.30	25.29	64.32	58.79	59.90	44.13
		2020 $\geq x(t)$	0.90	1.27	3.14	5.81	5.82	2.78	8.24	2.22	5.85	3.77
		2025 $x(t)$	32.85	13.86	28.73	23.13	65.71	26.84	65.83	59.41	59.49	45.88
		2025 $\geq x(t)$	0.92	1.30	3.21	5.95	5.96	2.84	8.44	2.27	6.00	3.86
		2030 $x(t)$	33.88	14.05	30.54	23.19	67.12	28.39	67.35	60.02	59.08	47.63
		2030 $\geq x(t)$	0.95	1.33	3.30	6.10	6.11	2.92	8.66	2.33	6.15	3.96
Vegetable Protein Supply	(g protein/cap/day/yr)	r	0.123	0.118	0.207	0.124	-0.055	0.187	-0.041	0.244	0.010	-0.006
		$\geq r$	0.017	0.020	0.028	0.053	0.021	0.023	0.027	0.021	0.029	0.027
		Adj. R^2	0.823**	0.766**	0.837**	0.336**	0.384**	0.866**	0.168**	0.927**	0	0
		2010 $x(t)$	48.12	48.36	51.41	37.99	42.27	50.10	42.83	45.28	34.72	36.28
		2010 $\geq x(t)$	1.54	1.76	2.46	4.63	1.86	1.99	2.33	1.85	2.57	2.34
		2015 $x(t)$	48.74	48.95	52.45	38.61	42.00	51.04	42.63	46.50	34.77	36.25
		2015 $\geq x(t)$	1.57	1.79	2.51	4.72	1.90	2.03	2.38	1.89	2.62	2.39
		2020 $x(t)$	49.35	49.54	53.48	39.23	41.72	51.98	42.42	47.72	34.82	36.22
		2020 $\geq x(t)$	1.60	1.83	2.57	4.82	1.94	2.08	2.43	1.93	2.68	2.44
		2025 $x(t)$	49.97	50.13	54.51	39.86	41.44	52.91	42.22	48.94	34.86	36.20
		2025 $\geq x(t)$	1.64	1.88	2.63	4.94	1.98	2.13	2.49	1.98	2.74	2.50
		2030 $x(t)$	50.58	50.72	55.54	40.48	41.17	53.85	42.01	50.16	34.91	36.17
		2030 $\geq x(t)$	1.69	1.92	2.70	5.07	2.04	2.18	2.56	2.03	2.81	2.57

3.1. Food Calorie Supply

Total Food Calorie

If the past pattern continues, the global total food calorie supply would grow at the annual rate of 13.43 ± 0.71 kcal/cap/day and reach 3210.4 ± 67.3 kcal/cap/day in 2030, representing an increase of 8.3-12.9% based on the current level (Table 1).

The annual increase of total food calorie in the developing countries (18.82 ± 0.92 kcal/cap/day) is expected to be about 3-fold of that in the developed countries (6.52 ± 1.30 kcal/cap/day). By 2030 food calorie supply in the developing countries (3241.4 kcal/cap/day) would close to developed countries' food calorie supply (3503.0 kcal/cap/day), an increase of 15.4% against 4.5% in the developed countries.

Total food calorie supplies for all of the regions are forecast to grow during the period 2010-2030 and, in most regions they are estimated to exceed 3000 kcal/cap/day after the years 2015-2020, with the exception of Africa and Caribbean. Food calorie supplies in Africa and Caribbean would continue to be lower and are forecast to reach 2656.9 kcal/cap/day and 2742.2 kcal/cap/day by the year 2030. If the past pattern continues, North & Central America would remain to be the greatest in food calorie supply and it is estimated to close to 4000 kcal/cap/day.

The following is the regional outlook of total food calorie supply in 2030 ($p < 0.05$): increase: Asia (12.8-20.5%), North & Central America (10.4-13.6%), South America (6.8-12.9%), Africa (5.9-9.4%); probably increase: Caribbean (-6.4-19.1%), Europe (-2.4-8.6%), Oceania (-2.6-4.5%).

Animal and Vegetable Sourced Calories

If the past pattern continues in the forecast period, global vegetable sourced calorie supply would grow at the annual rate of 10.49 ± 0.77 kcal/cap/day, equivalent to 3.5-fold of animal sourced calorie supply. Global proportion of animal sourced calorie in total food calorie supply is forecast to slightly increase to 16.8% in 2030.

For both animal and vegetable sourced calorie supplies, their annual rates in the developing countries, i.e., 5.49 and 13.33 kcal/cap/day/yr separately, are expected to be about 3-fold of that in the developed countries. By 2030 the animal and vegetable sourced calorie supplies are forecast to separately increase $34.7 \pm 12.0\%$ and $12.5 \pm 4.3\%$ in the developing countries and, in the developed countries the two values would be $4.3 \pm 10.5\%$ and $4.5 \pm 2.2\%$. Vegetable sourced calorie supply in the developing countries would be slightly greater than that in the developed countries by 2030. On the other hand, the animal sourced calorie in total food calorie supply of developed countries is estimated to remain a stable level of 27.3% in the forecast period, but in the developing countries this proportion would grow and reach 15.1% by 2030. The proportion for developed countries would be approximately 2-fold of that for developing countries.

Regional animal sourced calorie supply in 2030 is expected to have various outcomes ($p < 0.05$): increase: Asia (25.2-53.6%), South America (8.7-29.9%); probably increase: Africa (-7.3-15.0%), Europe (-12.8-19.9%); probably decrease: Caribbean (-49.1-29.2%), North & Central America (-6.5-6.0%); decrease: Oceania (-25.5- -8.2%).

The vegetable sourced calorie supply for all of the regions is projected to increase in the forecast period, with the highest growth in North & Central America (15.6%), and a lowest growth in Europe (2.9%) as compared to the current supplies. By 2030 the vegetable sourced

calorie supply in all of the regions would increase to about 2500 kcal/cap/day. At the same time the vegetable sourced calorie supply in North & Central America is estimated to be greater than 3000 kcal/cap/day.

Of these regions the proportions of animal sourced calorie for Asia and South America only are expected to increase during the period 2010-2030. In 2030 this proportion for Europe (29.7%), Oceania (22.8%), South America (22.7%), and North & Central America (20.3%) should be greater than Asia (16.2%), Caribbean (11.5%), and in particular Africa (7.1%).

3.2. Food Protein Supply

Total Food Protein

Total food protein supply in the world is forecast to grow at the annual rate of 0.33 ± 0.02 g/cap/day and reach 84.5 ± 1.8 g/cap/day by 2030, increasing $9.9 \pm 2.4\%$ relative to the current level (Table 1).

In the developed countries the total food protein supply would annually grow 0.49 ± 0.04 g/cap/day, about 2-fold of that in the developed countries. Total food protein supply in the developing countries is forecast to increase to 82.2 ± 3.3 g/cap/day in the year 2030 and in the developed countries it would reach 108.3 ± 5.1 g/cap/day, equivalent to the relative growths of $16.2 \pm 4.7\%$ and $5.1 \pm 4.9\%$ separately.

Total food protein supply in all regions, but not Oceania, is forecast to grow in the coming years. Asia (0.57 ± 0.04 g/cap/day/yr) is expected to have the highest annual growth and Africa (0.15 ± 0.02 g/cap/day/yr) and Caribbean (0.14 ± 0.10 g/cap/day/yr) would have the lower annual growth.

The total food protein supply in Oceania is estimated to slightly decline in the forecast period. By 2030, the total food protein supply in Europe and North & Central America would reach 110 g/cap/day, and in Asia, Oceania, and South America it would exceed 85 g/cap/day. Total food protein supplies in Caribbean and Africa are expected to only reach 65 g/cap/day by 2030.

The regional outlook of total food protein supply in 2030 is as follows ($p < 0.05$): increase: Asia (13.0-22.9%), South America (3.4-17.5%), North & Central America (5.3-11.3%), Africa (3.1-8.6%); probably increase: Europe (-0.8-12.5%), Caribbean (-10.7-20.9%); probably decrease: Oceania (-7.9-4.5%).

Animal and Vegetable Sourced Protein

Both animal and vegetable sourced protein around the world are forecast to grow, with the annual rates of 0.21 ± 0.01 g/cap/day and 0.12 ± 0.02 g/cap/day respectively. The proportion of animal sourced protein in total food protein supply for the world is expected to grow and increase to 40.1% in 2030. Compared to animal protein supply, the vegetable protein (50.6 vs. 33.9 g/cap/day) would continue to be the major food protein source for human food in 2030.

The developing countries would follow the similar trend with the world in the growth pattern of animal and vegetable sourced protein. The proportion of animal sourced protein in total food protein is estimated to increased to 34.5% in 2030. In the developed countries the animal sourced food protein supply would grow and reach 67.1 ± 6.1 g/cap/day by 2030, more than 2-fold of that for developing countries, but the vegetable protein supply is expected to

slightly decline in the forecast period (-0.06 ± 0.02 g/cap/day/yr). Animal sourced protein proportion for developed countries would grow and increase to 62.0% in 2030.

Excepting Oceania (-0.08 ± 0.06 g/cap/day/yr), all regions' animal protein supplies are expected to grow in the future. Asia and South America would have the higher annual rate (0.35 g/cap/day/yr). With the lower annual rates of 0.04 and 0.01 g/cap/day, Animal protein supplies for Africa and Caribbean are expected to slowly grow during the coming years.

Overall the regional outlook of animal protein supply in 2030 is expected to be ($p < 0.05$): increase: Asia (22.8-52.5%), South America (10.3-30.3%), North & Central America (0.8-8.9%); probably increase: Europe (-2.8-25.9%), Africa (-3.6-16.6%), Caribbean (-25.5-27.8%); probably decrease: Oceania (-13.2-7.0%).

Most regions' vegetable protein supplies are projected to increase in the coming years, with the exception of Europe (-0.04 ± 0.03 g/cap/day/yr) and South America (-0.01 ± 0.03 g/cap/day/yr). Among these regions Asia (0.21 ± 0.03 g/cap/day/yr) and North & Central America (0.24 ± 0.02 g/cap/day/yr) would have higher annual growths.

A regional outlook of vegetable protein supply in 2030 is outlined to be ($p < 0.05$): increase: North & Central America (8.0-17.2%), Asia (4.0-14.5%), Africa (1.6-9.6%); probably increase: Caribbean (-5.9-21.1%), Oceania (-7.5-8.8%); probably decrease: Europe (-8.1-3.8%), South America (-7.4-6.7%).

The proportion of animal sourced protein in total food protein is expected to increase and reach 35.5%, 61.6%, 56.8%, and 21.7% for Asia, Europe, South America, and Africa in the year 2030. In North & Central America, Oceania, and Caribbean this proportion would decline to 54.5%, 62.9%, and 36.4% in 2030.

4. Conclusions and Discussion

4.1. Conclusions

Global total food calorie supply is forecast to grow at the annual rate of 13.43 ± 0.71 kcal/cap/day and would increase to 3210.4 ± 67.3 kcal/cap/day in 2030. Vegetable sourced calorie supply in the world would grow at the annual rate of 10.49 ± 0.77 kcal/cap/day, which is 3.5-fold of that for animal sourced calorie. Global proportion of animal sourced calorie in total food calorie supply is estimated to slightly increase to 16.8% in 2030.

Total food protein supply in the world is forecast to grow at the annual rate of 0.33 ± 0.02 g/cap/day and would reach 84.5 ± 1.8 g/cap/day by 2030. Both animal and vegetable sourced protein around the world are forecast to grow, with the annual rates of 0.21 ± 0.01 g/cap/day and 0.12 ± 0.02 g/cap/day respectively. Global proportion of animal sourced protein in total food protein supply would grow and increase to 40.1% in 2030. Compared to animal protein supply (33.9 g/cap/day), the vegetable protein (50.6 g/cap/day) is expected to be the major food protein source in human food by 2030.

Total food calorie supplies for all of the regions would grow during the period 2010-2030. In most regions they are forecast to exceed 3000 kcal/cap/day after 2015-2020, with the exception of Africa and Caribbean. Total food calorie supplies in Africa and Caribbean are projected to reach 2656.9 kcal/cap/day and 2742.2 kcal/cap/day by the year 2030. If the past pattern continues, North & Central America would remain to be the greatest in food calorie supply and reach about 4000 kcal/cap/day. By 2030, the vegetable sourced calorie supply in

all of the regions would increase to around 2500 kcal/cap/day and it is estimated to exceed 3000 kcal/cap/day in North & Central America.

Total food protein supply in all regions excepting Oceania is forecast to grow in the coming years. Asia (0.57 ± 0.04 g/cap/day/yr) is expected to have a greatest annual growth and Africa (0.15 ± 0.02 g/cap/day/yr) and Caribbean (0.14 ± 0.10 g/cap/day/yr) would show the lower annual growth. Total food protein supply in Europe and North & Central America would reach 110 g/cap/day in 2030, and it would exceed 85 g/cap/day in Asia, Oceania, and South America. Total food protein supplies in Caribbean and Africa are expected to reach 65 g/cap/day by 2030. Excepting Oceania (-0.08 ± 0.06 g/cap/day/yr), all regions' animal protein supplies are expected to grow in the coming years. The proportion of animal sourced protein in total food protein supply for Asia, Europe, South America, and Africa is forecast to increase and reach 35.5%, 61.6%, 56.8%, and 21.7% respectively in the year 2030. In North & Central America, Oceania, and Caribbean, this proportion would decline to 54.5%, 62.9%, and 36.4% in 2030.

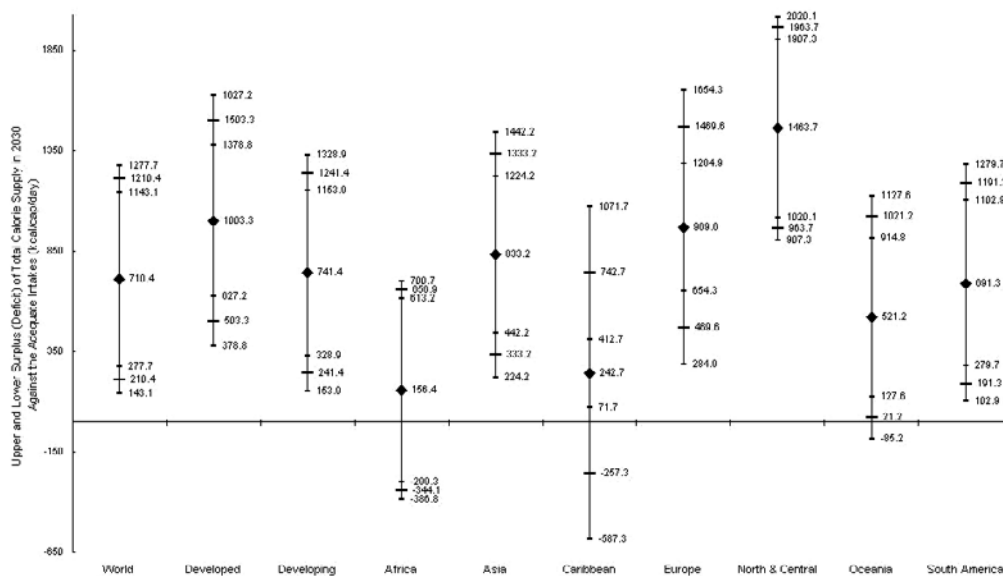
4.2. Balance of Food Nutrition Supply and Demand

Deficient and imbalanced intake of food energy and protein will result in malnutrition of the human beings. Malnourishment weakens people's immunity and strength, making them succumb more quickly to disease. For example, nearly 57% of malaria deaths are attributable to malnutrition¹. People living on a food with sufficient energy but deficient in food protein may suffer from retarded growth. In severe case, various diseases like Kwashiorkor, or even death is resulted. Overweight of body mass have been becoming the most important health problem in developed countries such as United States. Malnutrition will have a great impact on national economy, which results in annual losses of 6 to 10% in Gross Domestic Product (GDP) due to losses in labor productivity¹.

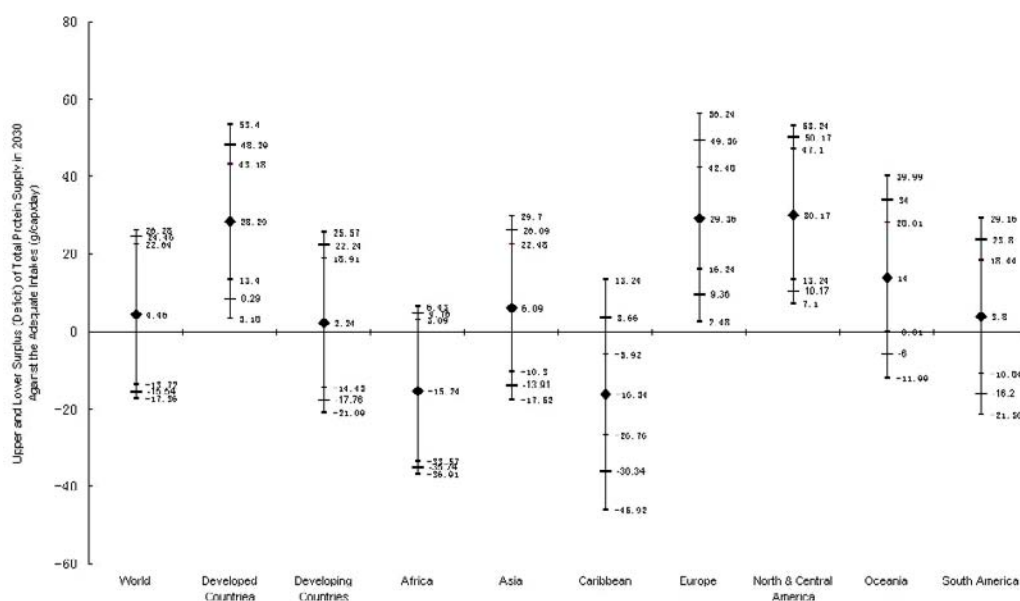
Adequate nutrition intakes must be defined to determine balanced food supply and demand. Adequate intakes of food energy and protein will change with the gender, ages, body mass, culture, social and economic conditions, etc. Some indices for adequate nutrition intakes have been developed in different countries. For example, the RDAs (Recommended Daily Amounts) for United States, and the PRI (Population Reference Intake) for Europe Union, and the DRIs (Dietary Reference Intakes) for China²¹. It is almost unlikely to formulate a unique and worldwide used criterion for balanced nutrition intakes. Summarized from various researches²¹⁻²⁴, the adequate intake of food calorie and protein may separately fall in the range of 2000-3000 kcal/cap/day and 60-100 g/cap/day.

According to the adequate intakes above, global food calorie supply would exceed the adequate energy intake after around 2015. Developing countries are expected to go beyond this range during the period 2015-2020. Food calorie supplies in the developed countries, Europe, and North & Central America have been greater than the upper threshold. Asia, South America, and Oceania would touch this ceiling in 2010-2015. Food calorie supply in Africa and Caribbean is in an adequate range and would not get beyond the range before 2030. In contrast to an early report by the FAO, which estimated that 56% of the human race lived in nations with average per capita food supplies of 2200 food calories per day or less²⁵, our forecasts suggest that in the coming years the focus should be put on the over-intake of food calorie for most regions (Fig. 1A). It seems that the tasks to reduce the proportion of

hungry people in half from 1990 to 2015, suggested by the Hunger Task Force in 2002¹, may likely be achieved by 2015.



(A)



(B)

Figure 1. Expected surplus (>0) or deficit (<0) of food calorie supply (A) and food protein supply (B) by 2030, against the adequate intakes (Food calorie: 2000-3000 kcal/cap/day; food protein: 60-100 g/cap/day). “—”: surplus (upper) or deficit (lower). “— — —”: 95% confidence interval of “—”. “◆”: the expected average.

World's food protein supply is estimated to be less than the upper threshold during the period 2010-2030. Food protein supply would be adequate in the developing countries before 2030. However in the developed countries, Europe, and North & Central America, the food protein supply have already exceeded the upper threshold. Asia, South America, and Oceania are estimated to run in the adequate range of food protein supply. Food protein supply in Africa and Caribbean is just a little greater than the baseline in the forecast period. As a consequence, food protein supply in these regions should be improved in the coming years (Fig. 1B).

Although malnutrition and hunger are currently more related to poverty and inequitable food access than to inadequate food production, particularly in Africa²⁶. Researchers in Africa emphasize, however, that the continent's social and economic problems remain a major obstacle to development²⁵.

Continuous adoption of high-yielding varieties that bred mainly by traditional breeding methods, has contributed to steady growth of crops yield and production since the 1960's²⁷. In addition to conventional breeding, recent developments in non-conventional breeding, such as marker-assisted selection and cell and tissue culture techniques, could be employed for crops in developing countries, even if these countries stop short of transgenic breeding¹⁴. By any way, major increases in crops production and yield must be achieved to meet the future demand for food worldwide, particularly in Africa and Asia⁹.

Demand for fishery products is also rising and it might double by 2040²⁸. However more than 60% of the world's major fisheries will not be able to recover from over-fishing without restorative actions. Declining fishery production in natural ecosystems has been partially offset by increased production through aquaculture and plantations^{8,29}.

The food production related development issues such as the loss of lands and biodiversity, the depletion of water resources, and the environmental and human health consequences of fertilizer and pesticide application are of growing concern^{9,15,20,26,30,31}. In particular, the expansion of agricultural lands deeps the climate changes and the loss of biodiversity. Fortunately the studies are being conducted to find solutions, e.g., genetic high-yielding crops breeding¹⁵, transgenic fish technologies⁸, etc.

In a strict sense, food nutrition includes not only calories and protein, but also various vitamins, mineral substance, trace elements, et al. All elements of food nutrition should be considered in future studies. Fruits (bananas, apples, oranges, et al.) are expected to become one of the major sources of food nutrients in the future.

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