STRUCTURE MODIFICATION OF POTATO SLICES TO REDUCE OIL ABSORPTION IN DEEP-FAT FRIED CHIPS

A Dissertation

by

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ABSTRACT

A consumer demand for healthier snacks has stimulated the scientific work on the issues of fat uptake on fried products. Most of oil absorption is a surface-controlled phenomenon, taking place when the product's structure is formed at the end of frying.

The first part of this study focused on evaluating different pre-treatments (soaking, dehydration, enzyme activation, sonication) associated with the calcium (Ca^{+2}) ion impregnation in potato tissue to enhance cellular-structure integrity during frying and its effects on oil absorption. The highest oil-content reductions were: 26.5% for "soaking" in $CaCl_2$ (20000 ppm / 30 min), 19% for "dehydration" in ethanol (70% v/v) + $CaCl_2$ (10000 ppm) for 2 minutes, 8.8% for "thermal treated" (50.0ºC/30min) + $CaCl_2$ (10000 ppm), 14.9% for "sonicated-assisted thermal treated" (50.0ºC/30min) + $CaCl_2$ (10000 ppm), and 30.2% for "sonicated-assisted soaking" in $CaCl_2$ (20000 ppm / 30 min).

The second part focused on optimization of ultrasound wave parameters to effectively delivery Ca^{+2} ions to the potato slices tissue as a pre-treatment to minimize oil absorption. At the maximum soaking $CaCl_2$ concentrations ($50x10^3$ ppm) and the longest time (30 min), sonicated samples showed a decrease of 43% in oil content when compared to the control.

The response surface methodology study estimated an oil content of 0.21 kg oil/kg DM for potatoes pre-treated in a $CaCl_2$ ($50.0\ x10^3$ ppm) solution for 16.5 minutes

(non-sonicated), and 0.16 kg oil/kg DM in a $CaCl_2$ (50.0 $x10^3$ ppm) solution for 23 minutes (sonicated).

Sonication made samples whiter in color (L*) and tougher to brake than the controls. Higher $CaCl_2$ concentrations yielded darker samples, higher bulk and solid densities, and higher degree of shrinkage for S/NS samples than the control ones.

Sensory evaluation of the control, non-sonicated, and sonicated samples found that the sensory quality attributes of "texture", "flavor", and "overall quality" were statistically significant ($p < 0.05$) among the treatments. The "sonicated" treatment scored the highest values for texture, flavor, and overall quality.

Sonication with calcium (Ca^{+2}) ion impregnation of potato tissue was effective in reducing the oil absorption of potato chips during deep-fat frying.

DEDICATION

To my mother, Heloisa Helena Fortes da Silva, my father, Paulo Cesar da Silva, my brothers, Rodrigo Fortes da Silva and Arlen Fortes da Silva, and my sister Ana Paula Fortes da Silva.

To my wife, Carmen Luiza Feitosa de Lima Gomes, and my in-laws, Luiz Clairmont de Lima Gomes and Heloisa Helena Feitosa de Lima Gomes.

For their unconditional support and love that provided me with the strength I needed during this journey. Gig'em!

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CHAPTER I

INTRODUCTION

In the USA, snack foods are becoming a major part of American's diet. Due to an ever-increasing busy life, snacking often plays an essential part in their daily meal. Snacking allows consumers to reserve energy for longer without needing time or space. However, as it is becoming a replacement for meal, attention has to be paid to the consumption of these products since they might pose a high impact on of consumers' health.

The *Dietary Guidelines for Americans,* a report published every 5 years by the Departments of Health and Human Services (HHS) and of Agriculture (USDA), contains nutritional and dietary information and guidelines for the public. It reinforces the evidences that healthy eating patterns and regular physical activity can help people achieve and maintain good health and reduce the risk of chronic disease throughout all stages of the lifespan. Among several key recommendations, reduction of overall caloric intake is suggested, focusing more in limiting the consumption of added sugars and fat (HHS-USDA, 2015).

Savory snacks are the top choice among Americans looking to satisfy their snack cravings. In 2017, salty snacks generated more than $27 billion in sales across U.S. retail stores (Nielsen, 2017b). Potato chips are the leader with 32% of sales, followed by tortilla chips (23%) and other salted snacks, according to IRI, Total US-MULO (MULti Outlet) (Thaler, 2018). Product innovation is helping drive the momentum in the salty

snack category in convenience. Customers are looking for familiar flavors with new twists, and nontraditional ingredients are growing in appeal (Nielsen, 2017c).

The relatively high oil content of potato chips, 35.3% to 44.5% w.b., is attributed to give the unique texture-flavor combination that makes them so desirable (Garayo and Moreira, 2002). In the last decade, many attempts to reduce fat content of potato chips were achieved by the use of vacuum frying technology. It has been established that a de-oiling step is crucial for processing of chips under vacuum conditions. Most of the parameters used to reduce oil uptake using this technology were physical, including centrifugation of the fried chips and pressurization rate of the frying vessel (Diamante et al., 2015; Garayo and Moreira, 2002; Moreira et al., 2009; Yagua and Moreira, 2011). These steps (centrifugation and pressurization) are applied just before the majority of the oil absorption phenomenon takes place, at the cooling stage. Significant oil reduction, 50% or more, when compared with atmospheric-pressure fried products, is not uncommon in many studies. Although these physical methods rely on removing most of the available surface oil, studies that focus on tissue-structure modification aiming to hinder the oil absorption phenomenon, are lacking in the literature.

Oil absorption is minimum during most of the immersion frying period, taking placing mostly during the cooling period when the product structure is formed. It is essentially a surface-related phenomenon resulting from the competition between drainage and suction into the porous crust once the food is removed from the oil (Bouchon et al., 2006b; Ufheil and Escher, 1996).

Moreira et al. (1997) explains that this surface phenomenon takes place when the food-product is removed from the hot oil (cooling stage) and the reason is the temperature difference between the fried-product and the ambient temperature. This change in temperature results in an increase of the pore's capillary pressure due to the increase of its surface tension. This will cause the oil to flow into the open pore spaces until equilibrium is reached.

This study suggests that the knowledge concerning the physical function of the cell wall components is useful to understand the changes in tissue structure and surface formation during the frying processing. These changes will affect structure and surface properties such as roughness, interfacial tension, pore size, and pore size distribution, which play a fundamental role on oil absorption of deep-fat fried products. Subsequent understanding of differences in the development of several other quality attributes such as texture, color, shrinkage, bulk and solid densities, porosity, and sensory properties are keys to successful product development.

During heating of potatoes, many changes will take place in their cellular components and structures. Starch granules within the cell absorb the cellular water and swell to form a gel. In general, the gelled starch remains within the cell, although some of the amylose may diffuse through the cell wall. Other major changes that occur are the loss of integrity of the cell membranes, resulting in a loss of turgor and the free diffusion of cellular contents throughout the tissue. Additionally, there is the effect of heat on the structure of the cell wall and the denaturation of protein, leading to a reduction in cell adhesion (Andersson et al., 1994).

Polysaccharides such as starch and cell walls provide much of the structure that gives a wide variety of foods desirable textural properties and other sensory attributes. Cellulose, pectic polysaccharides (pectin), hemicellulose, and glycoproteins are the major components in the cell wall of all plant foods. A rigid skeleton of cellulose microfibrils embedded in a gel-like matrix, mainly composed of pectic substances, hemicellulose and some protein, make up the structure of the cell wall. Each cell is "cemented" to each other by the lamella media, which is rich in pectin substances (Poovaiah et al., 1988). The main chain of pectin consists of poly-galacturonic acid in which the carboxyl groups are methyl-esterified to a large degree extent (Sterling, 1963). Depending upon their degree of methyl esterification, pectic substances are cross linked inter- and intra- molecularly by calcium to maintain integrity of the cell wall matrix and thus, are thought to be largely responsible for tissue rigidity of plants (Clarkson and Hanson, 1980; Grant et al., 1973). During heating process, depolymerization of pectin is promoted which then leads to a reduction in both mechanical strength of the cell wall and adhesion between cells (Buren, 1979).

Pectin, a major component of the cell walls and middle lamella of potato cells, plays an important role in determining the texture of both fresh and processed vegetable products (Van Dijk and Tijskens, 2000). Part of the pectin can aggregate through calcium biding to form the junction zones that hold a gel together. The higher the calcium level, the higher the number of pectin chains can be aggregated to form calcium-intermediated noncovalent gels (Jarvis, 1984). It has been widely reported in the

literature that calcium plays an important role in providing stability and mechanical strength to the cell walls (He et al., 2013; Knee and Bartley, 1981).

The use of calcium has widely been reported to confer rigidity and mechanical strength to plant cell walls (Cormack, 1965; Poovaiah et al., 1988; Sham et al., 2006; Stow, 1993). It has been recognized to function as an intermolecular biding agent that stabilizes pectin-protein complexes of the middle lamella in plant tissue (Demarty et al., 1984; Fry, 1986; Roux and Slocum, 1982).

Few studies have employed the used of calcium chloride as an aid to minimize oil absorption in fried-food products. Most of the studies focus on its use for improving texture of food materials, especially for fresh cut fruits and vegetables (Buren, 1979; Lovera et al., 2014). The food industry has many patents developed on pre-mixes for batter formulations where the addition of calcium chloride might have taken place. Usually the focus of these formulations are for coating, more as a surface treatment, forming a barrier for oil absorption (Mohamed et al., 1999). Usually, satisfactory results are obtained when calcium chloride is associated with the addition of hydrocolloids (Rimac-Brnčić et al., 2004). Hydrocolloid treatments may alter the water-holding capacity in the food material and consequently affects oil uptake (Pinthus et al., 1992).

The use of calcium ions has been used to minimize cell separation during cooking processes. However, most of the unit operations studied were on steam or boiling water-cooked potatoes, but not on deep-fat fried products.

Studies that make an effective delivery of calcium ions into potato tissue that result in suitable alternatives to control oil absorption of deep-fat fried foods are

suggested. These studies focus on methods for calcium impregnation such as soaking, thermal treatment for methyl-esterification of pectic substances for Ca^{+2} cross-linking, and partial dehydration combined with Ca^{+2} soaking treatments.

Evaluation of another method (ultrasound) to enhance the delivery of Ca^{+2} in to the potato tissue is also verified. A number of mechanisms by which ultrasound can affect mass transfer are possible (Haydock and Yeomans, 2003; Knorr et al., 2004). The most common ways sonication processing can enhance mass transfer are: cavitation (sponge effect) and microjet induced on the food material. It is very important that this processing alternative delivers of Ca^{+2} to the tissue adequately, without further degradation of the cellular material that could affect the oil absorption mechanism negatively. The physics behind the production of ultrasound waves and its various mechanisms for interaction with the food-matrix for specific processes can be found on the literature review (Chapter III) of this manuscript.

This study proposed the development of a process to promote cellular-tissue "stabilization" of potato slices through Ca^{+2} ion impregnation, prior to deep-fat frying. This method should be able to control oil absorption of the potato chips while keeping their quality attributes.

CHAPTER II

RATIONALE, SIGNIFICANCE, HYPOTHESIS, AND OBJECTIVES

2.1. Rationale

Deep-fat fried products constitute a major component of American's diet. Potato chips are the most consumed products, followed by tortilla chips. Improved public awareness of the desirability of reducing the fat content in the average diet has prompted study into means of lowering the oil content of many snack products.

Three decades ago, the potato chip industry considered the control and reduction of oil content to be of major importance (Gamble et al., 1987). However, little was known of how processing parameters could affect the final oil content of potato chips. A study to determine the relationship between moisture loss and oil uptake during frying of potato chips, and the influence of frying temperature and the effects on yield was carried out by Gamble et al. (1987). The researchers found that the loss of moisture and oil uptake were found to be interrelated. Both phenomena were found to be linear functions of the square root of frying time. Within the temperature range examined (145ºC, 165ºC, and 185ºC), moisture loss and oil uptake were independent of frying temperature. Moreover, based on the data acquired and visual observations of the process, they concluded that the amount of oil entering the potato slice is directly proportional to the amount of moisture lost and should depend on how the moisture is lost. The oil should lie in distinct areas where drying has occurred and, thus, should be in a small number of major sites and in very many small sites, with the edge containing excess amounts of oil.

According to the authors, oil enters the slice during frying and, probably to a greater extent, from the surface adhering oil being pulled into the slice when it is removed from the fryer due to condensation of steam producing a vacuum in the pore spaces. This hypothesis was proved to be not accurate by Moreira and Barrufet (1998) who stated that the main mechanism of oil uptake takes place during the cooling stage, thus the only mechanism is capillary pressure, not condensation. Further explanation of this phenomenon is described in more details in Chapter III.

Based on the mechanism proposed above by Gamble et al. (1987), the oil content will be low when moisture loss is slow and continuous without the formation of large surface-damage sites. Improved cellular adhesion, either in selection of tubers or by pre-fry treatment of slices, should reduce oil content if more moisture loss sites are formed. The production of small "holes" (pores) in the slice prior to frying will allow controlled moisture loss and should reduce the final oil content. It should be possible to produce potato chips of any required oil content by controlled pre-fry drying.

Pore size and pore size distribution formed during the frying process is the only mechanism for oil uptake (Moreira and Barrufet, 1998). Gamble and Rice (1987) already had some idea of these mechanisms when they mentioned "number of moisture loss sites" and size of "holes".

A processing technique used to reduce oil uptake employed steam during the finishing step. It involved conventional frying with premature removal of the product from the fryer at a high (10%) moisture content and finished the processing using super-heated steam (Krokida et al., 2001a). However, Gamble and Rice (1987) indicated that

an end of frying processing step may not be the best point of influence in the manufacture of a low-fat potato chips. The most clearly defined factor influencing oil uptake during potato chips production would have to do with the initial solids content of the tubers. It is known that a potato with a high solids content (mainly starch) will yield a potato chip with lower final oil content. It was believed that the initial solids content could be artificially increased by pre-drying potato slices prior to frying.

The first attempt to modify the structure of potato slices prior to frying was made by Gamble and Rice (1987). They assessed the effectiveness of pre-fry drying operations using hot air, microwave energy, and freeze-drying. Each of the drying processes used resulted in a distinct final moisture and starch gelatinization distribution in the final product, thus determining the final oil content and its distribution pattern. Microwave and hot air treatments resulted in a reduction in the final oil content by up 20%, which was related to the degree of pre-fry drying and gelatinization of the starch. Freeze drying resulted in an increase in the oil content, related to the initial moisture reduction and the lack of gelatinization of the starch. Oil distribution at the microscopic and macroscopic level was related to the initial moisture distribution in the slice (more uniform in air drying and freeze drying than in microwave drying). For all the treatments, the oil was present as small discrete droplets evenly distributed throughout the slice, with considerable association with cell walls. It was suggested by the authors that pre-fry drying could be the determining factor in reducing the final oil content of potato chips than the post-fry treatment mentioned above.

In attempt to evaluate particle size distribution on the oil absorption of tortilla chips, Moreira et al. (1997) used dry masa flour fractionated into fine, intermediate, and coarse particle sizes to make tortilla chips. Results showed that tortilla chips prepared from finely ground resulted in highest oil absorption and lower porosity; tortilla chips made from coarse particles, presented the lowest oil content; and intermediate masa produced tortilla chips with final oil content sitting in between them. Tortilla chips made from fine masa contained numerous small pores closer to the surface and few larger pores in the interior. Most of the oil filled the pores within the chips. Cross-sections of tortilla chips prepared from intermediate particle size flour produced larger and deeper pores than the tortilla chips made from fine masa. Most of the pores were filled with the frying oil. Coarse masa resulted in the formation of large pores within the tortilla chips. The oil filled some pores, but left many of them empty due to a decrease in capillary pressure within the larger pores. Capillary pressure is proportionally inverse to the pore diameter. The same authors also verified for the first time in the literature, at which stages of frying the oil absorption would take place. The chips absorbed only 20% of the total final oil content during frying, and 64% was absorbed during cooling leaving only 36% at the chip's surface. Initial moisture content significantly affected the final oil content of tortilla chips, as initial moisture content increased the final oil content increased. Scanning electron micrographs showed that pore size distribution developed during frying is the main cause for oil absorption during cooling. Small pores trapped more air during frying resulting in a higher capillary pressure during cooling and then higher final oil content. Although this study used flour to make masa as a model-food for

frying, which is different from a cellular matrix as in potato tissue, it did demonstrate the effect of the raw material structure on the oil absorption of the final food-product.

Kim and Moreira (2013) evaluated the effect of two pre-treatments, blanching and sodium chloride (NaCl) soaking, on the oil uptake of potato chips fried under atmospheric pressure. Chips blanched in hot water (85ºC / 3.5 min) had a 10.8% decrease in oil uptake compared with the non-blanched samples. Blanching alone had no significant effect on the oil content of the control samples. However, a 10–54% decrease in oil absorption was observed for the chips cooled for 0–60 s before de-oiling using a centrifuge system at 8.1 RCF. At higher centrifuge speed, 13.8 RCF, the pre-blanched chips had lower oil content only when cooled for 60 s after frying. The authors hypothesized that the high-centrifuge speed seemed to have an effect in the oil absorption characteristics of the blanched samples due to the forced convection cooling effect during the rotation of the chips in the fryer. Blanching causes a pre-gelatinization of the outer layer of starch, thus making a barrier to the oil ingress. However, contradictory findings exist in the literature.

The same authors (Kim and Moreira, 2013) found that pre-treating the potato slices with 3% NaCl solution had significant effect on the final oil content of the chips compared with the control; however, the difference was only 4%. De-oiling at lower centrifuge speed (8.1 RCF) without cooling resulted in 35% less oil content compared with only 10% when the chips were de-oiled at 13.8 RCF. Increasing the cooling time resulted in higher oil absorption as expected. Less oil absorption was observed by the chips de-oiled at 8.1 RCF than at 13.8 RCF. Compared with blanching, soaking in NaCl

solution resulted in lower oil absorption after frying. No explanation was given on how the of sodium chloride impacted the oil absorption. However, the authors claimed that changes in the structure of the pre-treated chips surface together with the forced convection cooling effect of the centrifuge could lead in less oil reduction from the product's surface.

Pedreschi et al. (2005) observed that blanching potato slices causes starch gelatinization, which results in a microstructure with significant influence on the increase of potato chips oil uptake after frying. Some authors reported that blanching (50 - 70ºC) before frying activates the pectin-methylesterase (PME) enzyme, and the resulting reactions decrease porosity and hence reduce oil (Aguilar et al., 2006). Alvarez et al. (2000) found that blanching potato strips before frying at higher temperatures for a short time (97ºC, 2 min) resulted in higher oil content than the control strips. At this temperature, the effect of the enzyme would be negligible since it would have been inactivated already. The physical barrier of pre-gelatinized starch and the activation of PME enzymes could be two independent factor playing major roles on the absorption of oil. Both mechanisms could lead to significant changes in the tissue structure of the potato, thus affecting the oil uptake mechanism. Detailed further investigation on this process is still needed.

Frying under reduced pressure is an efficient alternative method of reducing the oil content in fried foods while producing potato chips with the same texture and color of those fried in atmospheric conditions. It is defined as the frying process that is carried out under pressures well below atmospheric levels, preferably below 6.65 kPa (Da Silva

and Moreira, 2008; Garayo and Moreira, 2002). Lower pressures will lower the boiling point of water, thus during frying a lower frying temperature can be used, typically from 100ºC to 140ºC, whereas in conventional frying at atmospheric pressure, the typical range is from 165ºC to 180ºC. Much lower temperatures (less than 100ºC in vacuum) will still allow dehydration of the product; however, the gelatinization of the starch can be compromised. A complete and fast gelatinization of the starch is necessary for structure formation. It will allow for higher starch expansion during gelatinization. Its subsequent dehydration during the evaporation process, will allow it to harden, therefore settling the final structure of the chip.

Ways of removing the adhered surface oil, while the product is still in the fryer, has been the subject of many studies and patents for deep-fat frying processes. In the case of vacuum frying, this problem is exacerbated by the pressurization step. The pressurization step is necessary to equalize the pressure from inside the fryer to atmospheric pressure to open the fryer for product removal after being fried, This causes a quick increase in pressure in the pore space thus forcing most of the surface oil into the product pore spaces (Moreira et al., 2009).

For vacuum frying, a de-oiling mechanism is required to reduce the excessive oil absorption at the surface of the product. Da Silva and Moreira (2008) showed that the oil content of vacuum fried (1.33 kPa) sweet potato chips and green beans was 24% and 16% lower compared to traditionally fried products, respectively. However, vacuum fried blue potato and mango chips had 6% and 5% more oil, respectively, than the

traditional fried samples. These results clearly indicate that product characteristics, and texture developed during frying, can affect the final oil content of the product.

Troncoso and Pedreschi (2009) found that vacuum frying (5.37 kPa, 120ºC) increased significantly oil content of potato chips as compared to atmospheric frying (140ºC). The authors concluded that in vacuum frying the heat and mass transfer rates are higher than in atmospheric frying due to the decrease in the boiling point of water at vacuum pressure (5.37 kPa and T_{sat} = 34ºC). The pressurization step rapidly increases the pressure at the pores, causing the oil adhered at the chip's surface to penetrate in the food (until the pressure at the pores equals the atmospheric pressure. In comparison with conventional fried products, vacuum fried products have a more uniform pore size distribution and smaller pore diameters. More details are provided in Chapter III. Basically, it is due to the nature of the process, where moisture is removed uniformly from the product when under vacuum. Uniformly distributed pores with smaller diameters will suck more oil into its capillary structure when compared with less uniformly distributed and higher diameter pores. Therefore, some systems are required at the end of vacuum frying to control this potential higher oil absorption.

Many vacuum frying units are equipped with centrifuges for de-oiling the product after frying. The centrifuges are installed in a special vacuum dome attached to the vacuum fryer (Moreira, 2014; Pandey and Moreira, 2012). Vacuum frying can be used as an alternative to produce healthier snacks with lower oil content (Moreira et al., 2009). Garayo and Moreira (2002) showed that vacuum fryers could produce potato chips with lower oil content (30% less) and the same texture and color characteristics of

those fried in conventional (atmospheric) fryers. However, it is a rather expensive technique when compared with conventional frying processes. It requires the use of a bank of pumps to produce vacuum, a condensation system to trap the moisture evaporated from the products being fried, centrifuges to control oil uptake of the fried product, and it is a batch process. Compared to traditional deep-fat fried products, vacuum fried products have more uniform pore size distribution as well as smaller diameter pores. Smaller pores-diameters makes vacuum frying products to absorb more oil at the end of frying due to higher capillary pressure, thus requiring a de-oiling step to control oil uptake. The more uniform pore size distribution in vacuum-fried potato chips (Garayo and Moreira, 2002; Yagua and Moreira, 2011) makes it easier to remove the surface oil during the de-oiling process (Smith, 1992).

Processing parameters for conventional frying of potatoes such as temperature, time, type of tuber (cultivar and starch content), and thickness of the slices have been well studied to produce chips with high quality attributes (Gamble et al., 1987). Also, in some situations, those parameters were optimized with the final goal to decrease oil content to a certain extent. Very few studies were dealt with changing the cellular structure of tissues to obtain the same benefits as cited above (Krokida et al., 2001a). Most of these studies used blanching and dipping in salt solutions without much explanation on how these techniques would affect the cellular structure. To change this structure, a deep knowledge of vegetable tissue physiology is needed. This information can serve as a basis to develop the best approach to reduce oil uptake in potato chips during traditional as well as vacuum frying.

In most fruits and vegetables, including potatoes, the texture of the raw tissue depends on the presence of pectic substances, which are one of the components of the intercellular material. These substances are responsible for the adhesion of the cells within the vegetable tissue. Pectic enzymes produce free carboxylic groups, which can react with endogenous divalent ions, e.g. calcium and magnesium, creating more rigid structures and increasing firmness through cross-linking. Formation of calcium-pectates causes firming of the cell wall and increases middle lamella-cell wall rigidity (Bourne, 1989).

Based on this information, this study used exogenous di-valent ions such as calcium (Ca^{+2}) in potato slices to evaluate its effect on oil absorption during deep-fat frying of potato chips by retarding tissue degradation during the frying process. The impact on the quality attributes of potato chips was also evaluated.

2.2. Significance

The results from this project will open a new field in food engineering where new techniques (food-matrix engineering) can be utilized to accommodate raw materials to food processing operations that seek specific objectives, such as the reduction of oil absorption of potato chips. Lower-calorie chips should attract the attention of consumers demanding these types of snacks without compromising their quality attributes. By altering physically and/or chemically the structure of these raw materials, the control of the final product quality attributes such as color, texture, odor, and flavor should be more tunable by the manufacturing process. This technique will bring versatility to the use of

raw materials into the development of new products without the need of altering the already established conventional unit operations and equipment. Therefore, it is anticipated that this project would attract a great deal of interest not only from the scientific community, but also from the food industry.

2.3. Hypothesis

Oil uptake in deep-fat frying products is a structure-dependent phenomenon. Hence, ways of stabilizing the cellular matrix should reduce oil absorption of potato chips. The lamella media, which is responsible for cell intercellular attachment, contains pectic substances that can be cross-linked by using di-valent ions to stabilize the cellular matrix. Effective delivery of di-valent ions to specific parts of the raw potato tissue, before its final structure is formed, should prevent further cell de-attachment and/or rupture, thus decreasing the oil absorption of the final deep-fat fried product.

2.4. Objectives

The main goal of this study is to effectively delivery of calcium ions to specific parts of the potato tissue (lamella-media in inner cells) to stabilize the cellular material during deep-fat frying, thus minimizing the oil absorption while keeping the desirable potato chips quality attributes.

This study was divided into two parts. Part I refers to the evaluation of different techniques to reduce oil content in potato chips during frying. Part II studied the ultrasound to reduce oil absorption.

The specific objectives designed to achieve the main goal of part I were (see Figure 2.1):

I. Evaluate different pre-treatments to reduce oil uptake in potato chips:
    a. Soaking potato slices in Ca^{+2} solutions at different concentrations and time;
    b. Soaking the potato slices in alcohol to dehydrate the samples without shrinkage and also in combination with Ca^{+2};
    c. Employing heat for the activation of the pectin-methylesterase (PME) to increase the number of free carboxylic groups in the pectic substances in the lamella-media for further exogeneous Ca^{+2} crosslinking;
    d. Using ultrasound to further enhance Ca^{+2} delivery to the cellular matrix.

II. To select the best pre-treatment technique from Objective I

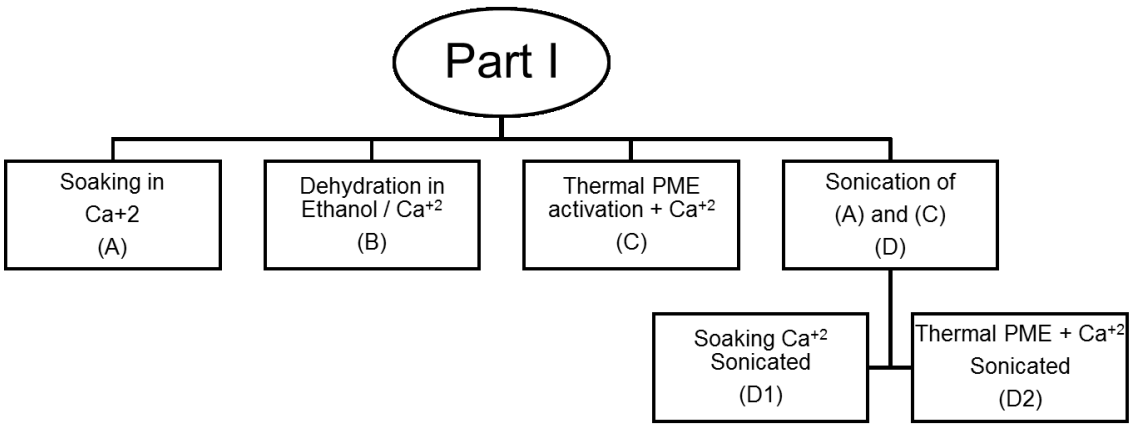


Figure 2. 1. Flow diagram of Part I studies.

The specific objectives designed to achieve the main goal of part II were (see Figure 2.2):

I. To evaluate the effect of sonication operating parameters (energy/time) in combination with the selected pre-treatment.

II. To optimize the pre-treatment parameters (soaking times, $CaCl_2$ concentration, sonication time/energy);

III. To evaluate the effect of pre-treatment and sonication processing on the final product quality attributes: texture, color, shrinkage, bulk density, solid density, and porosity

IV. To visualize structural changes in potato chips during frying;

V. To evaluate the sensory acceptance of the products by the general public on the following sensory attributes: appearance, color, odor, texture, flavor, and overall acceptance.

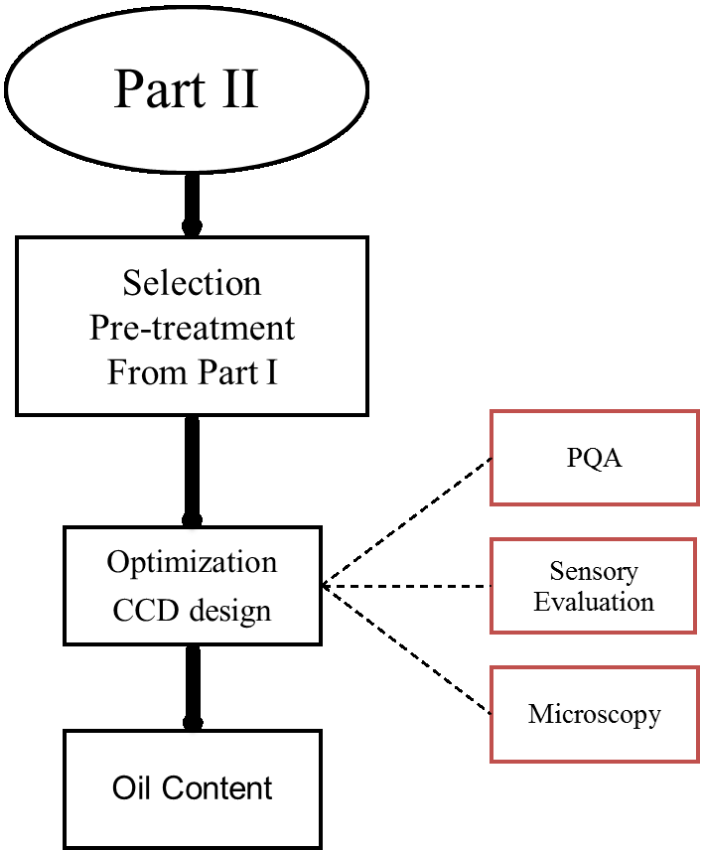


Figure 2. 2. Flow diagram of Part II studies

CHAPTER III

LITERATURE REVIEW

The literature review of this study focuses on: (i) deep-fat fried snack consumption in the US market and its implication on health (ii) advances in deep-fat frying, which includes: oil absorption, technologies for oil reduction, acrylamide control, mathematical modeling, and new approaches, and (iii) ultrasound technology: physics, production, measurements, applications, and mass transfer mechanisms.

3.1. The US market for fried snacks

Due to busy lifestyle, worldwide, and more specifically in the USA, snack foods are becoming a major part of American's diet. People can be seen eating small meals or "snacking" while in transit, whether they are driving a car, walking, commuting, on meetings, and so on. Snacks should serve as a source of calories and nutrition that should keep people going until the next opportunity to have a wholesome meal. But sometimes they can replace a meal entirely, also they can indulge, serve as a treat, a party staple, wellness (weight management or anxiety/stress reducer), and simply be fun.

According to Nielsen (2017e) retail data, global snack sales totaled $374 billion annually. Europe ($167 billion) and North America ($124 billion) make up the majority of worldwide snack sales, with sales flat in Europe, and growing at a rate of 2% in North America, compared to the previous year (Nielsen, 2017a). While annual snack sales in Asia-Pacific ($46 billion), Latin America ($30 billion), and the Middle East/Africa ($7

billion) are significantly lower than in the other two regions, annual growth in these regions increased more over the past year—4% in Asia-Pacific, 9% in Latin America and 5% in the Middle East/Africa.

Within the total snack category, salty snacks and fruit/vegetables brought in the largest share of retail sales. In the 52 weeks ending April 1, 2017, salty snack sales generated approximately 27.72 billion U.S. dollars. Salty snacks contribute more than one-fifth of snack sales in North America (STATISTA, 2017).

The snack food industry is very competitive and the savory and salty snack segment in particular shows a high market concentration. PepsiCo, Inc. captured a retail sales share of 36.4 percent in 2014 (STATISTA, 2018).

Figure 3.1 shows the sales of the leading potato chip brands of the United States in 2017 (STATISTA, 2018). Lay's® is the leading potato chip brand of the United States with about 1.7 billion U.S. dollars' worth of sales in 2017, accounting for approximately 29.6 percent of the potato chip market that year (STATISTA, 2018).

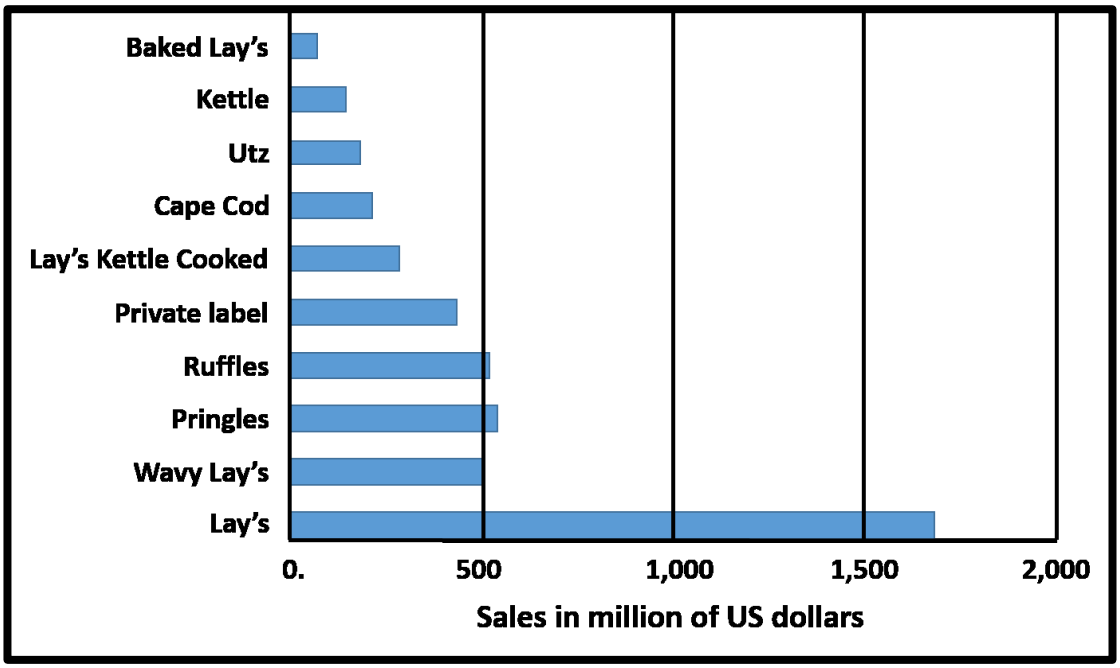


Figure 3. 1. Sales of the leading potato chip brands of the United States in 2017 - Reprinted from STATISTA (2018).

While growth is happening in a variety of traditional and healthy snack categories, products that call attention to specific healthful claims are driving the strongest uptick in sales. For example, snacking products that are non-GMO lead the way with an 18.2% surge in dollar sales for each of the past five years, followed by snacking products that are free from artificial colors/flavors (16.2%) and no/reduced sugar claims (+11.3%). Comparatively, the average snack product has seen an increase of only 1.2%. Even in traditionally indulgent snacking categories like salty snacks, health claims are driving sales (Nielsen, 2017d).

On a different work, (Nielsen, 2017b) reports that yet as consumers strive to make healthier life choices, convenience is still king. When shoppers make quick trips to

the convenience store, they are purchasing less healthy options, possibly because the healthy assortment they are accustomed to at conventional stores are not available. However, with 44.2% of consumers willing to pay premium prices at convenience stores, there is an opportunity to grow healthier snacking options in this channel.

3.2. Efforts for healthier snack choices

To keep the new developments in nutritional science current, every five (5) years, the U.S. Department of Agriculture (USDA) and the Department of Health and Human Services (HHS) examine the latest developments in nutritional science and release a new version of their "Dietary Guidelines for Americans". The "2010-2015 Dietary Guidelines for Americans", showed no changes to the recommended fruits and vegetables daily servings. However, they did emphasize the move to a more plant-based diet, specifically instructing Americans to fill half their plates with fruits and vegetables at every meal or snack as a way of simplifying the process of making sure Americans are eating enough. The document points out that most Americans of all ages consume too few fruits and vegetables and too many added sugars and solid fats. The 2015-2020 edition of the guidelines was released on 2016, and while the previous guidelines sets a high standard designed to reduce overall caloric intake, eat more nutrient-dense foods and increase physical activity, the current one focuses primarily on healthy eating patterns, making healthier choices across the lifespan, seeking variety, nutrient-dense foods, amount, limiting calories from added sugars and saturated fats, and reducing sodium intake.

These guidelines pose both challenges and opportunities for food engineers, scientists, technologists, and the food industry. A variety of fried snacks focusing on healthier choices can be seen nowadays in the shelves of most grocery stores around the country. However, some product quality attributes are overlooked or even not achieved on those products. Smaller food companies usually put products out on the market faster than bigger companies. Their products do not always go through rigorous validation process, in depth research for shelf-life, allowing them to put a variety of snack alternatives (exotic flavors, colors, shapes). The higher demand from the public, and the lack of choices on the shelves, drives the retailers to accept the risk of putting those products out on the shelves as trials and eventually gauge the sales from there.

Several studies on healthier choices of fried snacks using fruits and vegetables as raw materials were carried out in the last decade (Bingol et al., 2012; Da Silva and Moreira, 2008; Dueik and Bouchon, 2011a; Kim and Moreira, 2013). However, very few of them have used vacuum frying technology on their processes. One great advantage of vacuum frying is its versatility. You are able to fry different sources of raw materials, including almost any type of fruits and vegetables. Since it uses a lower frying temperature range when compared to conventional processes (frying under atmospheric pressure), this technology can prevent scorching of different sources of raw materials. Thus, the use of vacuum frying process makes it possible to obtain a final product with higher nutritional density when compared to conventional frying.

3.3. Deep-fat frying

Deep-fat frying of food materials have been around for a long time. It is rather a "simple" and popular technique used worldwide. Basically, raw food material is submerged into edible hot oil, fat or combination of those, at a rather high traditional food processing temperature range, that will lead to the dehydration and cooking of the raw food material.

This unit operation can be considered a rather complex operation, which involves simultaneous heat and mass transfer, resulting in counterflows of water vapor (bubbles) and oil at the surface of the piece (Bouchon et al., 2006b). This process can be divided into four distinct stages (Farkas et al., 1996). The first stage, initial heating, is the period of time during which the surface of the product is heated from its initial temperature to the boiling point of water; this period is usually short and a negligible amount of water is lost from the food. The second stage, surface boiling, is characterized by the sudden loss of water, the beginning of the crust formation, and a boiling convection regime due to high turbulence, associated with nucleate boiling. The falling rate period, the third stage, represents the period of time during which the bulk of the moisture is lost. It is the longest of the stages and the temperature of the core region approaches that of the boiling point of water. The bubble end point is the final stage and describes the apparent end of moisture loss from the product (Farinu and Baik, 2005; Singh and Debnath, 2011).

Deep-fat frying produces food-products with very process-specific attributes, the main ones being texture, flavor and color imparted by several chemical reactions

(Maillard reaction), and the mouthfeel produced by its rather high oil/fat content. Since the raw food material is heated while submerged into a hot fluid, the relatively high convective heat transfer coefficient and temperature will be the main determining factor for heat transfer, therefore the dehydration process is rather fast. Deep-fat frying can be categorized in three operating pressure ranges, they are mentioned in the following sections.

3.3.1. Conventional or atmospheric frying

This operation is carried out in open frying vessels under oil/fat temperature ranging usually from 165ºC up to 190ºC. Since it uses frying open vessels, frying is done under atmospheric pressure, and consequently at that temperature range will be above the boiling point temperature of the water contained in the food.

3.3.2 High pressure (Super-atmospheric)

In this system, frying operations are achieved on closed frying vessels, where the steam buildup is used to maintain and control higher pressures (2 atm). The main use of this process is for operations where certain quality attributes (color uniformity, tenderness, moisture retention) of food-products is desirable. The used of this processing technique is very common on chicken fried industry. One of the great advantages is that the heat transfer coefficient is substantially increased, sometimes it can be doubles if compared with an atmospheric pressure setting (Erdogdu and Dejmek, 2010).

3.3.3 Vacuum frying

In these closed systems, vacuum pumps are used to decrease the pressure inside the frying vessel. Pressures below than 10 Torr (1.33 kPa) are the most common used in

this system. This will result on a reduction of the boiling point temperature of the water within the material to be fried. At 10 Torr of pressure, the corresponding boiling temperature for pure water is 11.0ºC (51.9ºF). An operating temperature range of 100ºC to 120ºC is used in this process to assure doneness of the products (cooked). The major concern is the starch gelatinization, where it will take place around 60-75ºC. These products tend to have lower starch gelatinization compared to atmospheric frying. The rapid moisture loss during the process can result in less cooking with a number of intact starch granules (Ravli et al., 2013). To have complete gelatinization, water availability is fundamental. This has leaded consumers to perceive some vacuum fried products as being raw, not fully cooked. Depending on the type of product, especially those that are consumed in the raw state, like fruits in general and some vegetables (i.e. carrot), a great market opportunity for processed products appealing to be closer to its raw state, can be explored with vacuum frying. Also, the glycemic index, which is a relative ranking of carbohydrate according to how they affect blood glucose level, can be lowered since raw starch takes more energy to be metabolized. Starch gelatinization is responsible for the product "body/hard structure", ultimately leading to its texture.

One of the major advantages of vacuum frying is its versatility. Because it uses lower temperatures, the possibility to scorch products, or develop undesirable darkening in the product's surface due to extreme browning by-products from the Maillard reaction, is extremely reduced. This technique is suitable for fruits and vegetables with high sugar content and thermolabile components such as some pigments and vitamins. This opens a wide field for exploration of fried fruits and vegetables that could not be

used in conventional frying while keeping high quality attributes (color, texture, flavor, odor, oil content). This technology can be used to produce value-added (nutrient retention, color retention, and lower oil content) food products such as mango chips, green beans, sweet potato chips, blue potato chips (Da Silva and Moreira, 2008).

Another advantage of this technology is the reduction of potentially carcinogenic components that naturally occurs in any food which contains amino acids and reducing sugars undergone thermal process. One of them is acrylamide, which is classified by the International Agency for Research on Cancer as probably carcinogenic and neurotoxic to humans and carcinogenic in animals (IARC, 1994). Some researchers claim that "vacuum frying is the only technology available that can produce high quality potato chips with no acrylamide content (Granda et al., 2004).

Due to the use of low temperatures and low oxygen exposure, oil rancidity in vacuum frying is greatly reduced compared to conventional processes (Shyu et al., 1998).

3.4. Advances in deep-fat frying

3.4.1. Oil absorption

Regardless of the pressure range the frying operation is being carried out, after initial heating of the raw food material, as frying proceeds, inner product moisture is converted to steam and escapes vigorously through the product microstructure, creating selective weaknesses, including cracks, defects, open capillaries, and channels, in the cellular structure and membranes (Dana and Saguy, 2006). Some of this vapor may be

trapped within the pores due to restrictive intercellular diffusion and expand, becoming superheated, distorting the pore walls and contributing to product porosity (Moreira et al., 1995).

The mechanisms of oil absorption are not well explained on the scientific literature. Some authors have shown that most of the oil is confined to the surface region of the fried product (Bouchon et al., 2006a; Saguy et al., 1997) and there is strong evidence that it is mostly absorbed during the cooling period (Bouchon et al., 2006b; Moreira et al., 1997; Ufheil and Escher, 1996). While steam exists inside the food material and especially when it is vigorously escaping, it will serve as a barrier to prevent oil migration into the porous structure. Thus, oil absorption is minimum during most of the immersion period. Consequently, oil uptake is essentially a surface-related phenomenon resulting from the competition between drainage and suction into the porous crust once the food is removed from the oil (Bouchon et al., 2006b; Ufheil and Escher, 1996).

A more elaborated explanation for this phenomenon is given by other researchers (Moreira et al., 1997). Oil absorption is a surface phenomenon that takes place basically when the food-product is removed from the hot oil (cooling stage) and the reason is because of the temperature difference between the fried-product and the ambient temperature. This change in temperature results in an increase of the pores capillary pressure due to the increase of its surface tension. This will cause the oil to flow into the open pore spaces until equilibrium is reached.

A different explanation on the same subject (Gamble et al., 1987) states that the largest amount of oil is sucked into the product when it is removed from the hot oil and the vapor remaining inside will condensate, therefore reducing its volume and consequently causing a suction within the pores. Conversely, another study (Moreira and Barrufet, 1998) demonstrated that oil uptake in tortilla chips took place during the first 20 seconds of cooling, at which point the temperature of the product was still above the condensation temperature, suggesting that the effect of water vapor condensation is negligible. Moreira et al. (2009) had demonstrated that only 14% of the total oil content (TOC) is internal oil (IOC) while 86% is surface oil content (SOC) in fried potato chips. Almost 34% of the IOC and 0.7% of the SOC are absorbed during the first 20 s of frying operation.

Note that a fundamental difference between vacuum fried products and atmospheric fried ones, it is the type of porous formed. The surface tension, which is a function of the chemical make-up of the pore's walls, is similar between the two products. However, the physical size of the pores (diameter) and their distribution on the surface of the fried-product, are particularly different. Potatoes fried under vacuum will produce smaller pore-diameter which has higher capillary forces, consequently the suction action for surface oil will be higher compared to chip with higher pore-diameter sizes. But an interesting fact here is that products fried under vacuum will have a more uniform pore-size distribution, which facilitates greatly the removal of surface oil (Moreira, 2014; Smith, 1992).

3.4.2. Oil Reduction Technologies

3.4.2.1 Vacuum Frying

Vacuum frying has been considered a food processing technique that several studies claim to yield lower oil content products. For most of the cases, it is only possible when a centrifugation step of the final fried-product is introduced in the process, immediately after the fried-product is taken out from the hot oil. To improve its efficiency, centrifugation has to take place before atmospheric pressure is re-established within the vessel. Conversely, if this step is carried out after re-pressurization of the vessel, surface oil on the product will be forced into the pores of the fried-product while the system is being pressurized. Centrifugation after the pressurization step will be less efficient as it is harder to remove oil once it is within the pores.

Pandey and Moreira (2012) showed that a de-oiling system (centrifuge) removed up to 81% of the chip's surface oil when centrifuged for 40s at 750 rpm (84% at 300 rpm). They commented that short frying time and/or longer centrifuging time combinations would maximize oil removal from the chip's surface during the process. Less oil was absorbed by the potato chips when the fryer was pressurized at lower rate (25% open released valve) than at faster rate.

Mir-Bel et al. (2009) have demonstrated the influence of various parameters during the pressurization and cooling stages on the final oil content of fried potato and explained that oil absorption during the cooling stage is major. Others (Troncoso and Pedreschi, 2009) have described the kinetics of water loss and oil uptake during vacuum frying is influenced not only by the difference in temperatures, but also by the vacuum

break conditions as the system is restored to atmospheric pressure. They found that the volume of oil absorbed by the product is inversely proportional to the pressurization rate, meaning that lower velocities favors oil absorption showing an increase of 70% for potato chips compared to the oil content when the vacuum "breaks" abruptly.

3.4.2.2 Pre-treatments

Regardless of the three frying systems mentioned above, all of them have compromises. Sometimes they require pre-treatment of the raw product prior to frying to achieve specific desirable product quality attributes. Among them the most used are coating, blanching, pre-drying, and osmotic dehydration. Some post-treatments are more focused on oil uptake since it takes place mostly after the frying stage, at the cooling stage. Centrifugation, steam blast, hot air blast, and vertical placement of chips to allow for dripping of surface oil are among the most physical processes used to hinder oil uptake during the cooling stage.

The use of pre-treatments such as blanching, drying, freezing, osmotic dehydration, and coating are among the most employed pre-treatments in frying operations that have been used to preserve color, improve texture, and reduce oil absorption (Apintanapong, 2007; Diamante et al., 2011b; Krokida et al., 2001b; Nunes and Moreira, 2009).

During heating of potatoes, many changes will take place in their cellular components and structures. Starch granules within the cell absorb the cellular water and swell to form a gel. In general, the gelled starch remains within the cell, although some of the amylose may diffuse through the cell wall. Other major changes that occur are the

loss of integrity of the cell membranes, resulting in a loss of turgor and the free diffusion of cellular contents throughout the tissue. Additionally, there is the effect of heat on the structure of the cell wall and the denaturation of protein, leading to a reduction in cell adhesion (Andersson et al., 1994).

Pre-frying and post-frying treatments are mainly based on two important research findings: (1) the marked effect that crust microstructure development has in oil absorption, and (2) the fact that oil absorption results from the competition between drainage and suction into the porous crust once the food is removed from the oil bath and begins to cool down (Dueik and Bouchon, 2011a). In this regard, this results on a boundary issue. Most studies consider pre-treatments to focus mainly on alteration of surface properties, with the goal to decrease surface permeability and, therefore, oil uptake.

The various pre-treatments found in the literature can be classified into two major categories:

(1) *Conventional* - used in the past decades, the most studied includes blanching, pre-drying, osmotic dehydration, and coating;
(2) *Novel* - recent emerging technologies in food processing are being used also for pre-treatments of food products. It includes the use of ultrasound, infrared, microwave, and pulsed electric field.

Blanching usually uses steam or hot water (40ºC - 100ºC) for a rather fast surface thermal treatment of samples aiming to induce some gelatinization or prevent enzymatic (Yu et al., 2010) and non-enzymatic browning (Pedreschi et al., 2005), depending on the

temperature employed. Pre-starch gelatinization of the raw-product surface can decrease oil permeability, thus decreasing the oil content of the final product (Kim and Moreira, 2013). Longer periods of blanching may induce significant activation of pectin methylesterase enzymes (PME). PME can affect pore formation and texture if ideal conditions are met, such as availability of Ca^{+2} ions and optimum temperature range (40ºC – 70ºC). Low-temperature blanching, ranging from 40 ºC to 75 ºC, had been shown to improve the firmness of cooked vegetables and fruits, reducing physical breakdown and sloughing during further processing (Ni et al., 2005; Pérez-Alemán et al., 2005). Low-temperature blanching of sweet potatoes before steam cooking has shown significant increase in tissue firmness and cell wall strengthening (Abu-Ghannam and Crowley, 2006). He et al. (2013) showed that sweet potato slices blanched at 60ºC for 30 min and treated with 400 ppm Ca^{+2} prior to steam cooking resulted in the lowest free starch rate of about 7.0%, while the free starch rate without treatment was 12.8%, and the free starch rate of the samples blanched for 3 min at 100ºC and blanched for 90 min at 60ºC were 11.28% and 10.64%, respectively. Pectin-methylesterase (PME), naturally present in many fruits and vegetables including sweet potato, had the potential to play a major role in cell wall strengthening at low blanching temperatures. The authors concluded that low temperature blanching assisted by Ca^{+2} significantly increased the tissue firmness and strengthened the cell wall to resist the shear destruction in the mill, thus reducing the free starch rate during flour processing. PME can catalyze the hydrolysis of unesterified carboxyl groups in pectin molecules and induce cross-linking between carboxyl groups and calcium ions, therefore improving tissue firmness (Buren,

1979). Some authors claimed that blanching could also improve textural qualities of products, such as French-fries (Aguilar et al., 2006).

Pre-drying of food products using hot air or oven has been also reported to reduce oil uptake of fried food products. Cruz et al. (2018) pre-dried potato slices in an air recirculation oven (UF55PLUS Memeert, Germany) for 0, 10, 20 and 30 min at 60 ºC prior to fry at 190ºC. The highest oil content reduction was found for pre-dried samples (21%) when compared to the control. The authors claimed that higher moisture samples had the higher fat content due to its longer time in the fryer. Pedreschi and Moyano (2005) evaluated the effect of the pre-drying treatment over the texture evolution and the oil uptake of blanched potato slices (in hot water at 85 ºC for 3.5 min) during frying. Blanched potato slices were used as the control. Some blanched slices were additionally air-dried until reaching moisture contents of ~60 g/100 g potato (wet basis) - (slices blanched - dried). Either only blanched or blanched - dried potato slices were fried at 120, 150 and 180 ºC until reaching final moisture contents of ~1.8 g/100 potato (wet basis). Both the frying temperature and the pre-drying treatment had a significant effect ($p < 0.05$) over the final texture and oil content of the fried potato chips. When frying at 120ºC, potato chips were crispier and contained more oil (24% increase) than potato chips fried at 180ºC. Pre-drying dramatically decreased the oil absorption (22% reduction) and significantly increased ($p < 0.05$) the crispness of the blanched potato slices after frying. However, the authors gave no explanation on the effect of pre-drying on oil uptake.

The most clearly defined factor influencing oil uptake during chips production is the initial solids content of the tubers (Lulai and Orr, 1979). A tuber with high solids content will yield a chip of low final oil content (Gamble and Rice, 1987). The initial solids content can be artificially increased by pre-drying the potato slices prior to frying. However, it is not always the case as cited above. The surface and structure properties will play a major role on oil uptake. Other researchers (Jia et al., 2018) have showed that the type of pre-dehydration (air, vacuum-microwave, and infrared) can be a determining factor on the oil uptake of fried products. They evaluated water distribution (associated with cell wall, cytoplasm water, vacuole water) through low field nuclear magnetic resonance. For the same moisture content, depending on the type of dehydration carried out (convective, penetrating, surface conduction), different water distribution could be achieved, resulting in different patterns for oil absorption.

Osmotic dehydration (OD) is another method that aims to reduce initial moisture from the samples prior to frying, but also it can be used to increase the solute concentration in specific samples. Nunes and Moreira (2009) used maltodextrin to increase solid content of mango slices through osmotic dehydration, prior to vacuum frying. Frying temperatures and OD times had a significant ($p < 0.05$) effect on the oil content in mango chips. The lowest oil content in the chips (0.22 ± 0.01 w.b.) was produced with 70 min OD and vacuum frying at 120 ºC, and the highest value (0.30 ± 0.00 w.b.) with 45 min OD and a vacuum-frying temperature of 138 ºC. Longer OD times (60 or 70 min) produced chips with a more compact structure (due to water losses) which increased the mango slices specific gravity thus leaving less space for oil uptake.

Moreno and Bouchon (2008) evaluated different dehydration pretreatments on oil absorption of deep-fat fried potato cylinders. Samples were blanched in hot water and dried until a moisture content of 62% (w.b.) by either freeze-drying, air drying, or osmotic drying with a sucrose solution. Control (blanched) and dried potatoes were deep-fat fried at 170 °C from 1 to 5 minutes. Compared to the control, freeze dried samples increased oil uptake by 15.4% whereas air-dried samples reduced it by 11.2%. Similarly, osmotic dehydrated samples showed a high reduction in oil uptake compared to the control, up to 27%. However, this high decrease in oil absorption was attributed to the increase in solids content occurring during the osmotic dehydration process rather than a reduction in the amount of oil taken up. In fact, when the amount of oil absorbed per cylinder was determined, it was verified that oil uptake of osmotically dehydrated samples was even higher than the control, as opposed to what has been previously reported in the literature by other authors. These results highlight the importance of selecting an adequate basis to carry out comparisons properly.

Coating is the addition of edible ingredients, mostly in form of batter, to the surface of food raw material. It aims to improve texture, color, flavor and ultimately control oil and moisture content in fried foods. Significant interests are captured by the scientific community and the food industry sector to find the adequate formulation design, film forming polymer properties, and components to improve adhesion and active properties. Hydrocolloid-based coatings are among the most popular methods in the food industry. They can reduce the excessive oil uptake due to their unique thermo-

gelling properties and at the same time they are invisible and have no negative influence on the sensory attributes of fried foodstuff (Kurek et al., 2017).

The effectiveness in moisture retention and reduction of fat uptake of different edible coatings on a fat-free starchy product was determined by Mallikarjunan et al. (1997). Mashed potato balls were used as model food system. Samples were coated with corn zein (CZ), hydroxypropyl methyl cellulose (HPMC) or methyl cellulose (MC) film-forming solutions. Uncoated samples were used as control. Compared to the control, a reduction of 14.9%, 21.9% and 31.1% in moisture loss from the product was observed for samples coated with CZ, HPMC and MC films, respectively. Similarly, a reduction of 59.0%, 61.4% and 83.6% in fat uptake by the product was observed for samples coated with CZ, HPMC and MC films, respectively.

Hydrocolloid edible coatings reduce the oil content of deep-fat-fried food either acting as a lipid barrier when formed as thin films and dried before frying or by their gelation properties during heating (Kulp, 2011). Some of commercially available coatings are Fry Shield™ - calcium pectinate that is aimed to reduce fat uptake during frying fish, potatoes, and other vegetables and Seal gum, Spray gum™ - calcium acetate that prevents darkening of potato during frying.

Durán et al. (2007) coated potato slices with 16 g /L of edible film solution of hydroxypropylmethylcellulose (HPMC) prior to deep-fat frying. Contrary to expected, the potato samples coated with HPMC absorbed more oil than the control. They explained that the presence of hydroxypropyl groups could have limited the coating capacity forming of the film. Coating has also been reported to have an effect on the heat

transfer coefficient during frying of foods. Potato strips coated with hydrocolloids (gellan gum and guar gum) and fried in fresh soybean oil (170ºC / 100 s), were found to significantly reduce the heat transfer coefficient compared to the control (Kim et al., 2011). The authors explained that hydrocolloids produced water vapor bubbles during frying, which hindered heat transfer from the oil to the surface of the food, thus reducing the heat transfer coefficient. They also investigated the effects of the hydrocolloids on the oil content of potato strips and reported that there was 41% reduction in oil content compared to the control when the potato strips were coated with 0.9% guar gum. They further discovered a correlation between the heat transfer coefficient and the oil content of the potato strips ($R^2 > 0.99$). They stated that the decreased heat transfer coefficient led to reduced oil uptake during frying. However, this statement could be misleading, perhaps the "bubble shield", which consequently decreased heat transfer, was the main factor in hindering oil absorption as far as moisture evaporation was taking place at the surface of the potato strip samples.

Amaral et al. (2017) showed that coating potato strips with alginate (20 g/L) prior to frying (180 ºC/ 6 min) had no significant effect on the content of acrylamide in fried potato strips. However, a recent study showed that addition of low concentration of chitosan (0.27%) to batters can reduce the acrylamide content in fried batters by 59% (Sansano et al., 2016). The amino group of chitosan significantly competes with the amino group of asparagine in binding with the carbonyl group of the reducing sugar during frying, thus leading to reduction in acrylamide content of fried batters.

Ultrasound waves, more specifically high power (low frequency) ultrasound, induces mechanical, physical and chemical/biochemical changes through cavitation, which supports many food processing operations such as extraction, freezing, drying, emulsification and inactivation of pathogenic bacteria on food contact surfaces (Awad et al., 2012). The physics behind the production of ultrasound waves and its various mechanisms for interaction with the food-matrix for specific process can be found in more detail on the "Ultrasound" section of this literature review. Ultrasound pre-treatments were performed at 28 and 40 kHz and drying pre-treatments were conducted at 80ºC for 8 and 15 min prior to deep-fat frying at 150, 170 and 190ºC. They observed that, compared to the control, oil uptake of samples pre-treated with both ultrasound and drying significantly decreased ($p < 0.05$). It was concluded that at all the frying temperatures, samples pretreated with ultrasound had lower oil uptake in comparison with control samples (non-sonicated). Mohammadalinejhad and Dehghannya (2018) investigated various ultrasound frequency-time combinations on quality characteristics of potato strips during deep-fat frying. Results indicated that the potato strips subjected to ultrasonic waves at the frequency of 40 kHz for 30 min, exhibited the highest moisture diffusivity, resulting in the highest reduction in oil uptake (23.2%) among all the samples. Additionally, the ultrasound combined frequencies of 28 kHz (for 20 min) and 40 kHz (for 10 min) showed the best performance in reducing the shrinkage of fried products.

Infrared (IR) radiation (wavelength of 0.78 to 1000 μm), generates heat waves that can be effectively absorbed by food materials, the IR waves encompasses the

portion of the electromagnetic spectrum that borders on visible light and microwaves (Krishnamurthy et al., 2008). Food systems are complex mixtures of different biochemical molecules, biological polymers, inorganic salts, and water. The infrared spectra of such mixtures originate with the mechanical vibrations of molecules or particular molecular aggregates within a very complex phenomenon of reciprocal overlapping (Halford, 1957).

Infrared have been used in the food industry for drying, peeling, inactivation of microorganisms, blanching, and roasting of agricultural products. The suitability of using infrared (IR) heating as a dry-blanching pretreatment prior to frying, and investigation of its potential to reduce the oil uptake in French fry production has been evaluated by Bingol et al. (2012). They IR dry-blanched potato samples were fried at 146, 160, and 174°C for 1, 3, 5, and 7 min. At the end of 7 min frying, compared to non-blanched samples, dry-blanched samples had 37.5%, 32% and 30% less total oil at the frying temperatures of 146, 160 and 174°C, respectively. The final moisture contents of non-blanched and dry-blanched samples were between 50% and 60% after 7 min frying. A high oil absorption rate at the initial frying stage was observed for the IR dried blanched samples, mainly due to the dry-surface resulted from infrared dry-blanching. Non-blanched samples, which had higher moisture contents, had higher water vapor pressure during frying thus hindering oil penetration in the crust of the French fries. During infrared blanching, the formation of an elastic whitish skin was observed when the surface temperature was higher than 60ºC. The authors concluded that the reduced oil uptake of infrared blanched samples in the later stages of frying was due to both

gelatinization of the inner core and the formation of the crust, which together protected the inner layers from absorbing oil and mainly also due to the formation of the elastic whitish skin which decreased the diffusion rate of oil. More use of infrared can be found in other food processing areas (Bagheri et al., 2016; Huang, 2004; Li et al., 2014; Wang et al., 2017).

Microwave heating takes in consideration the absorption of energy from a microwave field by the food, resulting in internal heat generation and as a consequence internal vapor generation. The internal vapor generation leads to the development of a pressure gradient, which increases the rate of moisture transfer significantly as compared to conventional heating methods. Microwaves offer tremendous advantages, such as time, space, energy and nutrient savings, in certain food processing operations (Barutcu et al., 2009).

Most of the studies performed using microwave technology used it as a heat inducing source for frying of food products rather than for pre-treatment. Ngadi et al. (2009) evaluated the effect of a microwave pre-treatment at different time duration on the mass transfer of chicken nuggets during deep-fat frying was studied. Coated chicken nugget samples, pre-treated in a microwave oven for 1–2 min, were fried at 160 °C for times ranging from 0 to 300 s to evaluate the mass transfer as compared to the samples without a microwave pre-treatment. Microwave pre-treatment had a significant effect on moisture loss and oil uptake of chicken nuggets during deep-fat frying. They observed that microwave pre-treatment reduced the initial moisture content from 1.22 to 0.82 kg/kg d.b. and 2.48 to 2.01 kg/kg d.b. for coating and core layers, respectively. After

frying at 300 s, the moisture content of coating layer reduced from 1.22, 0.99 and 0.82 kg/kg d.b. to 0.40, 0.37 and 0.35 kg/kg d.b. for microwave pre-treatment times of 0, 1 and 2 min, respectively, while the moisture content of core layer reduced from 2.48, 2.26 and 2.01 kg/kg d.b. to 1.80, 1.77 and 1.71 kg/kg d.b. for microwave pretreatment times of 0, 1 and 2 min, respectively. The oil content kinetics for microwave pre-treated samples, both in the coating and core layers showed significant reduction compared to the control (without pretreatment). There was a 26.22 and 33.51% reduction in final fat content of the coating as a result of microwave pretreatment for 1 and 2 min, respectively, compared to the control. The trend shown for the core was quite similar, with a reduction of 10.95 and 16.66%, respectively. The authors claimed that this may be attributed to the reduction in moisture content of the nuggets and structural change with a modified moisture distribution during microwave pretreatment, which subsequently influenced fat uptake. There was pre-gelatinization of the chicken nuggets during microwave treatment, which might also be partly responsible for structural change that influenced fat uptake.

Belgin Erdoğdu et al. (2006) investigated the effect of microwave precooking of potato strips on the resultant acrylamide levels in French fries. Control and microwaved (10, 20, and 30 s at 850 W) samples were fried at 150, 170 and 190 ºC for predetermined times. Surface and core temperatures of potato strips were acquired during frying, and acrylamide content in the surface and the core regions were determined separately. The results showed that microwave application prior to frying resulted in a marked reduction of acrylamide level in the surface region, whereas a slight increase was noted for the

core region. When the potato strips were subjected to frying after a microwave pre-cooking step, acrylamide content in the whole potato strip was reduced by 36%, 41%, and 60% for frying at 150, 170, and 190 ºC, respectively, in comparison to the control. The findings of this study indicated that microwave precooking was effective in reducing acrylamide levels in the surface region of French fries, where most of the acrylamide formation takes place. The reduction of acrylamide in the surface of the microwave pre-treated samples was attributed, along with reduced frying times, to the lower surface temperatures attained during frying of these samples (measured). It was observed that the longer the microwave pre-treatment time, the lower the surface temperature during frying, and hence less acrylamide formation in this region. Maybe due to the change in potato structure as a result of precooking.

Cooked potato tissue has been reported to be more permeable, presenting less resistance to mass transfer (Grob et al., 2003). Consequently, it may have resulted in an increase in the rate of diffusion of water from the interior to the surface. As more water is supplied from the interior, more of the energy transferred from the hot oil to the potato strip will be extracted to vaporize that water, and this will prevent the surface temperature buildup. Even though the temperature of the core regions of all samples was slightly above 100°C for the duration of frying experiments, acrylamide formation in the core region upon frying was found to increase slightly with increasing microwave treatment time. The authors attributed these findings to a faster drying of the interior of the microwave-treated samples, resulting in the favorable conditions for Maillard reaction (in terms of moisture content) to develop sooner during the frying process.

Microwave preheating was reported to potentially lead to increased acrylamide levels in baked cut potato products due to the microwave removing moisture before oven baking (EU-Report, 2003). In summary, the authors have shown that the reduction of acrylamide was a consequence of the combined effects of reduced frying time and surface temperature. Water transport rate from the interior during frying was shown to play an important role in limiting acrylamide formation in the surface region.

Pulsed electric field processing (PEF) applies very short voltage pulses (in μs) with a high electric field strength to a product placed between two electrodes. PEF processing at low electric field strengths between 0.2 and 1 kV/cm for 0.1 to 10 ms can disrupt plant tissues without a significant increase in temperature (Faridnia et al., 2015; Lebovka et al., 2002). Electric fields between parallel plate electrodes are quasi homogenous. However, parallel plate electrodes do not produce a homogenous electric field when the sample to be treated has a heterogeneous composition and an irregular shape (Ivorra and Rubinsky, 2007). It has been widely used in the food industry for drying (Gachovska et al., 2009), freezing (Jalté et al., 2009), inactivating microorganisms (Amiali et al., 2004), and extraction (Bobinaitė et al., 2015; Ricci et al., 2018).

Liu et al. (2017) evaluated the effect of pulsed electric fields on the structure and frying quality of “kumara” sweet potato tubers. With respect to frying quality, tubers pre-treated with PEF at electric field strength of 1.2 kV/cm and fried at 190 °C showed significantly ($p < 0.05$) lower oil uptake (18%) than the non-PEF treated samples (22–23%). The reduction in oil content in PEF treated samples was due to the higher vapor

pressure difference between untreated and PEF treated samples, as PEF treatment increases the porosity of samples allowing within sample vapor to move to the surface of the sample at a much higher rate. Higher vapor flow rates result in fewer voids within the sample for oil to enter was the explanation given for the reduced oil content of the PEF treated samples.

These results in line with some of the results found by Janositz et al. (2011). In a study to evaluate the impact of PEF on the diffusion characteristics of potato slices, they concluded that PEF treatment on cell material led to pore formation in cell membrane and thus modified diffusion of intra- and extracellular media. A higher release of cell liquid during drying of PEF treated potatoes was noticed in comparison to untreated potato slices, where PEF treatment (1.8 kV/cm) reduced the oil content by 38.66% for fried potato strips.

Ignat et al. (2015) also found that PEF treatments (18.9 kJ/kg, 9000 pulses at 0.75 kV/cm and 810 pulses at 2.5 kV/cm) reduced the uptake of oil when compared to water dipped and blanched potato fries' samples. The increased smoothness of cut surfaces, caused by PEF treatment, may also lead to a decrease in oil content due to better draining of the oil after frying. In addition, PEF-induced electroporation might also cause the loss of cytoplasm from cells into the extracellular space, resulting in more water being located outside the cells, creating a barrier to oil uptake and hence reduce oil uptake during frying (Ignat et al., 2015).

In summary, several examples of conventional and novel pre-treatment methods using different technologies were reviewed with different results for oil uptake. Some

are more suitable for specific materials and others are more generalized. Examples of pre-treatment and results of some agricultural products for frying, using most of the conventional and novel methods explained here can be found in the review of Oladejo et al. (2018).

In deep-fat fried products, the crust is the result of several alterations that mainly occur at the cellular and subcellular level in the outermost layers of the product, where the temperature exceeds 100^{o} C. These chemical and physical changes include physical damage produced when the product is cut and a rough surface is formed with release of intracellular material, starch gelatinization and subsequent dehydration, protein denaturation, breakdown of the cellular adhesion, water evaporation and rapid dehydration of cells located in the forming crust, and oil uptake itself (Bouchon and Aguilera, 2001). Regarding cell integrity, evidences have accumulated that the majority of the inner cells retain their individuality (Reeve and Neel, 1960). As for the outer layers, where the crust is formed, cells seem to shrink during frying, with no extended rupture, whereas cell walls become wrinkled and convoluted around dehydrated gelled starch (Bouchon and Aguilera, 2001; Marle, 1997; Van Marle et al., 1992).

Three distinct microstructures are found in finished commercial French fries: (1) a thin outer layer (approx. 250 μm) formed by remnants of cell walls of broken or damaged cells by cutting; (2) an intermediate layer of shrunken intact cells that extends to the evaporation front, and (3) the core with fully hydrated intact cells containing gelatinized starch. The crust only extends over the outermost layer in French fries, around 1 mm (Aguilera and Gloria, 1997).

The crispy, porous, and oily outer layer or crust is the region where most oil is located and its structure plays a major role for oil absorption (Aguilera and Gloria, 1997; Costa et al., 2008; McDonough et al., 1993).

Since potato chips is formed of a crust only (0.5 - 1.0 mm thick and 2% of moisture or lower), structure forming is paramount on dictating how oil will be absorbed during and after deep-fat frying.

Characterization of changes in potato tissue during cooking in relation to texture development has been extensively studied (Marle, 1997). The use of ions of calcium has been the main factor to minimize cell separation during those cooking processes. However, most of the unit operations studied were on steam or boiling water-cooked potatoes, but not on deep-fat frying products. Calcium ions can assist in the formation of calcium-pectate bridges, thus firming the cell walls and increasing middle lamella-cell wall rigidity (Buren, 1973).

An effective delivery of these ions to the potato tissue should prevent further degradation of the cells by the frying process, thus controlling oil absorption.

3.4.2.3 Structure formation

Oil migration during deep-fat frying into the structure of deep-fat fried products can only be controlled if a fundamental understanding of the structure is acquired. It has been reported in numerous studies that most of the oil is absorbed in the cooling stage, at the end of frying, when there is very little moisture left in the fried product (< 2% w.b.), and its structure is formed. Durán et al. (2007) found that when potato chips are removed from the fryer, 35% of the oil remain in the surface whereas 65% penetrates into the chip

microstructure. These results are in agreements with those found by Moreira et al. (1997) who reported that only 20% of the final oil content was absorbed during frying and that almost 64% of the total oil content was absorbed during cooling, therefore remaining only 36% of the total oil at the tortilla chips surface. Since most of the oil is absorbed only at the end of the process, this suggests that oil uptake and water removal are not a simultaneous phenomenon.

Frying is a rather complex process of heat and mass exchange that induces chemical and physical transformations in the food that results in its unique structure. Moisture leaving the food makes cells shrink at first, then will expand, and escape the food-product through the surface. During this process, simultaneously physicochemical and structural changes in carbohydrates, proteins, fats, including starch gelatinization and protein denaturation will induce changes in membrane permeability, induce alterations in cell wall architecture, all of which will contribute for its specific porous structure.

Few studies in the past decade have focused on observing microstructural aspects of the frying of potato chips using more sophisticated technologies. Microstructure studies included oil location, cell walls and surface morphology as the main targets. Pedreschi et al. (2008) used Confocal Laser Scanning Microscopy (CLSM) on potato chips fried in thermoresistant fluorescent Nile Red dye to make optical sections in the samples at different depths without having to section them. Results showed that oil in the surface layers of potato chips were located preferentially around the cells, in their walls, covering most of the intercellular spaces. Dhital et al. (2018) used a broad range of

microscopy techniques and labelling methods to capture potato cell microstructure and fat distribution at different length scales. Two types of samples were evaluated, a fabricated potato chip (FPC), which was prepared from precooked and dried potato in form of flakes or powder, combined with pre-gelled and raw starches (so-called co-texturizers) and water to form a dough that was cut into discs and subsequently fried. The other sample was just regular raw potato slices cut into discs and subsequently fried into potato chips (PC). It was found that a significant proportion of the fat in fried PC was associated as thin film with the potato cell walls both at the surface and within the structure, while it is present as droplets at the fabricated chip surface (FPC). By frying isolated cells, they found movement of oil going to inside the potato cells. Enough evidence that the cell wall structure was damaged, was gathered. They concluded that such damages would potentially allow oil movement in potato chips tissue as well. Zhang et al. (2018b) investigated the oil absorption behavior of potato chips by combing dyed-oil methods, digital photo analysis, confocal laser scanning microscopy, and low field nuclear magnetic resonance imager. They observed that the oil was distributed along the contours of the cells, adhered to the cell wall, filling the cell interstitial, which agreed with the same findings by Bouchon et al. (2006a) and Pedreschi et al. (2008).

The plant cell wall is a highly organized composite that may contain many different polysaccharides, proteins, and aromatic substances. These complex matrices define the features of individual cells within the plant body (Carpita et al., 2001). Pectin is a major component of primary cell walls of all land plants and encompasses a range of galacturonic acid-rich polysaccharides. Three major pectic polysaccharides

(homogalacturonan, rhamnogalacturonan-I and rhamnogalacturonan-II) are thought to occur in all primary cell walls. These three polysaccharide domains can be covalently linked to form a pectic network throughout the primary cell wall matrix and middle lamellae. This network has considerable potential for modulation of its structure by the action of cell wall-based enzymes (Willats et al., 2001b). A schematic of the cell wall can be found in Figure 3.2.

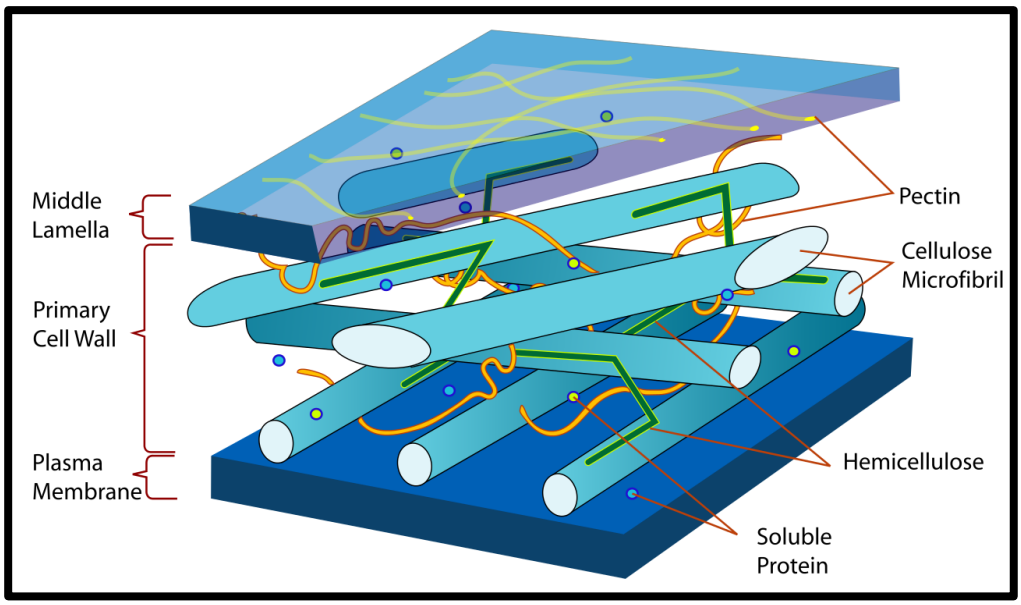


Figure 3. 2. Plant cell wall structure - Reprinted from LadyofHats (2007).

The pectic network influences the pH and ionic status of the matrix and, through its capacity to form gels, is also intimately involved in the generation of mechanical and porosity properties of cell walls (Willats et al., 2001a). The pectic network in the regions of the middle lamella has roles in intercellular adhesion and bonds linking middle

lamella pectin to pectin within primary cell walls (Knox, 1992). As such, the pectin-rich middle lamella is the major physical mediator of cell adhesion and separation as well.

Pectin polysaccharides are galacturonic acid polymers and are represented by three major types: homogalacturonan (HG), rhamnogalacturonan-I (RG-I), and rhamnogalacturonan-II (RG-II) (Atmodjo et al., 2013). The middle lamella between two cells is rich in pectin; its levels and chemical modification are key to regulating adhesion. Modification of pectin affects its ability to gel and act as glue between cells. HG pectin is gelled by calcium-mediated crosslinking. Newly delivered HG-pectin is highly methyl-esterified which makes it more fluid (viscous). The activity of a wall-modifying protein, pectin methyl-esterase (PME), removes the methyl groups of HG. De-esterified HG is readily cross-linked by calcium leading to a stiffer material and altering the mechanical properties of the cell wall (Braybrook et al., 2012; Micheli, 2001; Peaucelle et al., 2011; Willats et al., 2001a). PME activity can be counteracted by the activity of another family of cell wall proteins, pectin methyl-esterase inhibitors (PMEIs) and as such the balance of these two proteins and their activities have effects on the mechanical properties of the middle lamella. A model for cell adhesion and cell separation is presented in Figure 3.3.

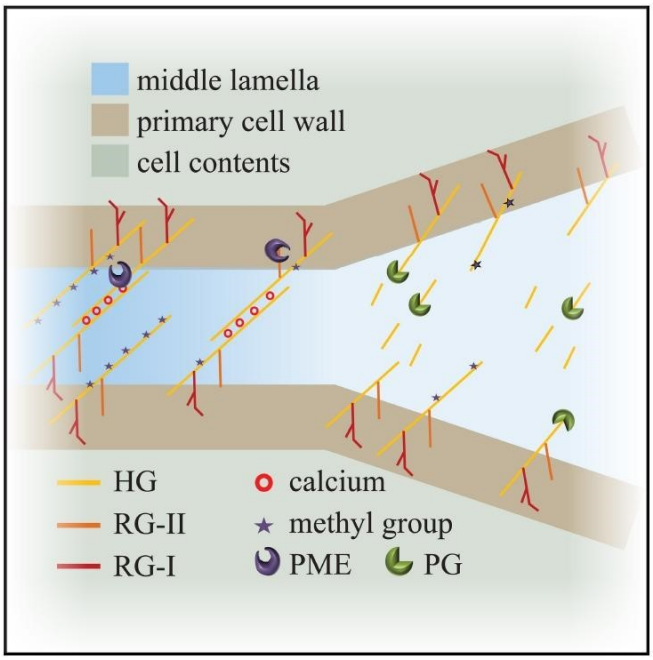


Figure 3. 3. Model for cell adhesion and cell separation - Reprinted from Daher and Braybrook (2015).

Cross-linking of the de-esterified pectin polymers maintains cell adhesion at the level of the middle lamella. Degradation of the de-esterified pectins by enzymes like polygalacturonases weakens connections and leads to cell separation. HG: homogalacturonan; RG: rhamanogalacturonan; PME: pectin methyl-esterase; PG: polygalacturonase.

Homogalacturonan pectin, in its de-esterified or low esterified form, is found in the middle lamella and in the corners of cell junctions (Bush et al., 2001; Guillemin et al., 2005; McCartney and Knox, 2002; Parker et al., 2001). Since de-esterified HG tends to form Ca^{+2} gels readily it is also important to note that calcium ions are enriched in the middle lamella (Bush et al., 2001; Huxham et al., 1999; Rihouey et al., 1995). The role of HG-Ca^{2+} gels in cell adhesion is underscored by the effects of treatment with calcium

chelators such as EDTA (ethylenediaminetetraacetic acid), HMP (sodium hexametaphosphate) and CDTA (1, 2-Diaminocyclohexanetetraacetic) which result in cell separation in various plant tissues (Letham, 1960; McCartney and Knox, 2002; Ng et al., 2000).

PME activity is a key control point for both the assembly and disassembly of the pectic network. The activity of PMEs is also highly regulated. Solution pH has been shown to affect the activity of PMEs in persimmon and apple tissue (Alonso et al., 1999; Denes et al., 2000) and PME activity is also salt dependent (Jolie et al., 2010). To make the situation more complex, it is important to recall that PME activity can be counteracted by PMEI proteins (mentioned above). It seems that in the field of plant science, there is still very little information on how most of the PMEs are specifically regulated and very little idea about their specificity. However more evidence that adhesion and separation are complex processes keeps surfacing, worthy of more studies (Daher and Braybrook, 2015).

Due to the complexities of these polysaccharides and enzymes, the even greater complexity of the plant cell wall, and numerous experimental difficulties in working with these polysaccharides and enzymes, much remains to be learned in establishing detailed structure-function relationships both for biological and technological process such as deep-fat frying.

A comprehensive review of how pectic polysaccharides are able to affect diffusion through the cell wall by determining cell wall porosity, the stability of calcium-

pectate gels, degree of methylation and ionic strength can be found in the literature (Marle, 1997).

Few studies relate how impregnation of metal ions and other solutes in plant tissue have resulted in lower oil absorption of fried products. Some of the possible explanations are related to structural properties of these fried products, such as surface roughness, interfacial tension, and crust porosity.

The soaking process of potatoes strips in NaCl (3% w/w and 50 min soaking time) solution led to a lower oil uptake (22%) compared to the control (Bunger et al., 2003). This same trend was also observed in the results of the factorial design, where higher NaCl concentrations and longer soaking periods reduced the remaining sensory oiliness.

Rubnov and Saguy (1997) reported in a study of a restructured potato product, that addition of fructose reduced the oil uptake. They claimed as the water evaporates, fructose concentration on the surface increased, enhancing crust formation. The crust was permeable to water leaving as steam, however, it probably acted as a barrier to oil absorption. Although it was not measured, the researchers also explained that the added fructose reduced oil uptake due to a change in interfacial tension, so that the wetting angle between product and frying substance increased. They also carried out apparent fractal dimension analysis derived from the silhouettes of the sample contour, it was related to surface ruggedness. A linear effect of the added fructose on reducing the ruggedness value from 1.27 to 1.08 was found. The apparent fractal dimension correlated linearly with oil uptake, suggesting a practical criterion for predicting oil

uptake during deep-fat frying. Utilization of the apparent fractal dimension is not novel, however its application for oil uptake prediction in various food systems has not been reported. Note that surface roughness has been assumed by many researchers in the field of frying to affect oil uptake. However, no data were available to quantify such effects. Rubnov and Saguy (1997) suggested the marked relationship between surface ruggedness and oil uptake certainly relates oil absorption to a surface phenomenon.

3.5. Acrylamide and frying

Thermal processing is an important treatment for food preservation, especially in the manufacture of shelf-stable foods with specific nutritional properties. In addition, it is indispensable for determining the sensory properties, in particular color, texture, and flavor in fried, baked, and roasted products (Gökmen, 2016).

Heat induces chemical change and a plethora of new molecules are generated in foods, some of which have been claimed to impart negative health effects. It may lead to the formation of heat-induced toxic compounds, so-called thermal process contaminants, that exhibit carcinogenic, and in some cases mutagenic properties, such as heterocyclic amines, and acrylamide (Skog et al., 1998; Tareke et al., 2002).

The first report for acrylamide in food-products was made by Swedish scientists (Tareke et al., 2002), it attracted world-wide attention, due to the fact that acrylamide is classified as probably carcinogenic to humans (IARC, 1994). They found that potato chips and French fries contained levels of acrylamide that are hundreds of times higher than what United States Environmental Protection Agency and the World Health

Organization consider safe for drinking water, which is limited to 0.5 μg of the acrylamide monomer per liter of drinking water. Studies with laboratory-heated foods revealed a temperature dependence of acrylamide formation. Moderate levels of acrylamide (5−50 μg/kg) were measured in heated protein-rich foods and higher contents (150−4000 μg/kg) in carbohydrate-rich foods, such as potato, beetroot, and also certain heated commercial potato products and crispbread. Acrylamide could not be detected in unheated control or boiled foods (<5 μg/kg) (Tareke et al., 2002). Which suggests that its formation takes place in temperatures above the boiling point of water at atmospheric pressure, 100ºC. Working independently, scientists from Norway, Sweden, Switzerland, the United Kingdom and the United States of America, have found that the amino-acid Asparagine when heated at certain temperatures in presence of reducing sugars results in acrylamide production (FAO/WHO, 2002).

Acrylamide is formed via the Maillard reaction as a result of the reaction between the amino acid asparagine and reducing sugars (glucose and fructose). Potatoes contain relatively high levels of both asparagine and reducing sugars and therefore potato products such as potato chips, French fries and roasted potatoes can contain high levels of acrylamide. However, the concentration of precursors can differ considerably not only between potato varieties but also with storage conditions. When those conditions for formation of the precursors cannot be controlled any further, attempts to find processing conditions to control acrylamide formation can be made.

Several studies have been made to control the amount of acrylamide produced in these carbohydrate-rich products that uses relatively high processing temperature ranges.

The approaches are focused in the processing temperature, time, and in the removal or transformation of the precursors.

Granda et al. (2004) evaluated means of reducing acrylamide in potato chips by using vacuum frying technology. The author compared frying temperatures (150°C, 165°C, and 180°C) at atmospheric pressure to vacuum frying temperatures (118°C, 125°C, and 140°C) at reduced pressure (10 Torr). It was concluded that frying under vacuum (lower temperature range) reduced acrylamide reductions up to 94%.

Some attempts to reduce the frying time using different technologies can reduce acrylamide formation. Ultrasonic microwave-assisted vacuum frying (USMVF) has been reported as a novel frying technique to produce potato chips at shorter frying period at lower frying temperature ranges (Ya et al., 2018). USMVF markedly increased the moisture evaporation kinetics and effective moisture diffusivity, reducing 20-28% of the drying time compared with the microwave-assisted vacuum frying (MVF)., at lower frying temperatures (90ºC – 100ºC). Although in this work the acrylamide formation was not measured, it is known that its formation is at temperatures of 100ºC or below is undetected (Tareke et al., 2002).

Reduction of acrylamide formation by selective removal of the precursor asparagine using the asparaginase enzyme in thermally treated starchy-food is also reported in the literature. In a study (Dange et al., 2018), potato slices were prepared and treated with different concentrations of L-asparginase enzyme viz. 0.2 IU, 1.0 IU, 1.5 IU and 2.0 IU respectively. The treated slices along with the control sample (not enzyme-treated) were subjected to deep-fat frying at 190ºC/6 minutes. It was observed that the

acrylamide formation was drastically reduced to 0.019 ppm in the chips treated with 2.0IU enzyme concentration as compared to untreated control chips in which acrylamide formation was 15.65 ppm.

Enzymatic mitigation of acrylamide formation combined with some additives (NaCl and citric acid) in deep-fat frying (180ºC) of potatoes is shown in another study. The synergistic effect of asparaginase with additives was evaluated. Asparaginase was effective in cleaving the asparagine for mitigation of acrylamide without significant changes in reducing sugar content during frying of potato slices. Also, the addition of additives along with asparaginase showed increased reduction (74%) in acrylamide formation (Aiswarya and Baskar, 2017).

Pedreschi et al. (2004) studied the reduction of acrylamide formation in potato chips was investigated in relation to frying temperature (150°C, 170°C and 190°C) and three pre-treatments before frying. (soaked in distilled water, blanched in hot water, and immersed in citric acid solutions). Glucose content decreased in ~32% in potato slices soaked in distilled water with an average reduction for acrylamide formation of 27%, 38% and 20% at 150°C, 170°C and 190°C, respectively, when compared against the control. Blanching reduced on average 76% and 68% of the glucose and asparagine content compared to the control. Potato immersion in citric acid solutions reduced acrylamide formation by almost 70% for slices fried at 150°C. For the three pre-treatments studied, acrylamide formation increased dramatically as the frying temperature increased from 150°C to 190°C. Blanching the potato slices before frying decreased the levels of precursors in this other study (Viklund, 2007). It was an efficient

way of reducing the acrylamide content; blanched potato chips contained 51-73% less acrylamide when compared with non-blanched samples. Blanching also resulted in similar acrylamide levels in potato chips from potatoes stored at 4°C to those in potato chips from un-blanched potatoes stored at 8ºC (Viklund, 2007). Zhang et al. (2018a) also determined the effect of combinations of blanching parameters, including blanching temperatures ranging from 65 to 85ºC and duration times ranging from 2 to 10 min, on reducing sugars, asparagine, acrylamide, and color levels of fried potato chips. It was found that certain blanching parameters resulted in optimal maximum reductions of 64.2, 49.8, and 61.3% for reducing sugar, asparagine, and acrylamide, respectively.

Patents and studies on the effect of polyvalent cations to reduce acrylamide formation in thermally processed snack foods and bakery products were developed (Elder et al., 2004; Lindsay and Jang, 2005). The potential formation and degradation of acrylamide during heating in the presence of monovalent and divalent cations was investigated by (Gökmen and Şenyuva, 2007). Dipping potatoes into calcium chloride solution inhibited the formation of acrylamide by up to 95% during frying without adversely affecting the sensory quality of fried potato strips (in terms of color and texture). The inhibition was attributed to the presence of monovalent or divalent cations rather than to the reduction of acrylamide precursors by dipping. Gökmen and Şenyuva (2007) postulated that the presence of Ca^{+2} would prevent the formation of the Schiff base of asparagines, and thus of acrylamide, during heating.

According to Gökmen and Şenyuva (2007), the sensory quality of fried potato strips, in terms of golden yellow color and crispy texture, was not adversely affected by

this Ca^{+2} treatment. Similar results were found by Mestdagh et al. (2008) who showed that dipping potato slices in $CaCl_2$ solution mitigates acrylamide formation, although only a marginal decrease was observed at the lowest concentration level (0.025 mol/L). As opposed to Gökmen and Şenyuva (2007), a crispier texture and a bitter aftertaste at higher Ca^{+2} concentrations were perceived by panelists. Mestdagh et al. (2008) confirmed that soaking potato slices in NaCl solutions significantly decreases the acrylamide content and reported that the oil content is also significantly reduced (27%) by NaCl addition (0.1%) to the blanching water. Acrylamide formation has been shown to decrease upon lowering the oil content of the potato model system, probably from a lower heat transfer from the oil to the system due different structure properties of the potato tissue. Therefore, decreased oil uptake seems a possible mechanism behind acrylamide reduction in the NaCl-treated potato chips. It is interesting that several additives, such as organic acids, NaCl, and Ca^{+2} were able to lower the absorption of oil when frying. This fits perfectly with the ongoing consumer trend to move toward healthier and low-fat products in order to counteract obesity and coronary heart diseases (Mestdagh et al., 2008).

The effectiveness of calcium and magnesium, as $CaCl_2$ and $MgCl_2$, respectively, to reduce acrylamide formation in tortilla chips fried in soybean oil during 30 s at 190°C was evaluated by Arámbula-Villa et al. (2017). Acrylamide was reduced to 69%, 70%, and 74% by adding 0.04, 0.08, and 0.12 M of $MgCl_2$ solutions to prepare the masa, compared with the reductions in 52%, 67%, and 52% obtained using 0.04, 0.08, and 0.12 M of $CaCl_2$, respectively. The color, oil absorption, and the fracture force of tortilla

chips using $CaCl_2$ were similar to those of the control. In contrast, tortilla chips with added $MgCl_2$ were dark and not as hard as the control. These results are in contrast to Mestdagh et al. (2008), which reported a reduction on the oil content of fried potato chips. However, there is a difference between those studies, the material is different, but does not have a cellular structure like potato tissue. This could be an indicative that these ions play an important role in the structure formation and its impact on oil absorption, whereas in masa it did not make any difference. Some other issues with the addition of ions in the oil might be addressed, such as the rate of oil degradation during frying and the consequent more rapid oil turnover rate (Mehta and Swinburn, 2001; Padilla, 2015).

A comprehensive review regarding mitigation strategies to reduce acrylamide formation in Fried potato products is found in the work of Morales et al. (2008).

The results of the present studies mentioned above indicate several factors that are important in minimizing the content of acrylamide formed in potato chips. In order to mitigate it, potato variety, storage conditions, temperature, time, addition of cations, and removal or transformation of precursors through enzymatic, soaking, and blanching processes, are crucial.

3.6. Modeling deep-fat frying process

Empirical curve fitting of experimental data can be categorized as one of the simplest descriptions of the frying process (Baumann and Escher, 1995; Kozempel et al., 1991). Many models have been based on simple diffusion, several approximations to account for evaporation and sometimes ignoring evaporation altogether. These models

are very process and product specific, any alterations on the physical properties or environmental conditions would make the model unreliable since it cannot be generalized.

Perhaps the first model to include simple conduction of energy and simple diffusion of moisture on a frying process was of Rice and Gamble (1989). One limitation on their approach is that they did not include the evaporation in the domain. Other simple diffusion models (Dincer and Yildiz, 1996; Moreira et al., 1995; Williams and Mittal, 1999) also calculated temperatures using only the diffusion term in the energy equation and did not account for the evaporation in the domain as well. Ateba and Mittal (1994) considered separate diffusion equations for energy, moisture, and oil phases, without any evaporation term in the energy or moisture transport equations. Only surface evaporation as a boundary condition for the energy equation was included. The rate of surface evaporation was equated to the rate of diffusive moisture loss at the surface. Kozempel et al. (1991) attempt in mathematically describe the deep-fat frying process modeled moisture loss using diffusion equation, Fick's second law. Using experimental data for oil temperature and product moisture content, an effective diffusivity, as a function of oil temperature, was determined. For the most part, those models could reasonably match experimental data, however most of the physics on transport phenomena was not addressed properly, or at least they have been disregarded.

Many of the first mathematical models of frying processes were limited to empirical and semi-empirical relationships for heat and mass transfer. The transient temperature and moisture profiles inside the food during frying was accounted for, and

there has been little research on the factors that influence the rate of crust development. All transport mechanisms were lumped into an effective thermal conductivity or an effective moisture diffusion coefficient.

A two-region model with a sharp boundary separating the core and the crust region was presented by Farkas et al. (1996). This can be recognized as a significantly improvement when compared to the simple diffusion models cited above. Frying was considered by this author to be a complex form of the Stefan class of problem. The generalized Stefan heat transfer problem is characterized by the presence of a moving interface, which divides two regions of distinct physical and thermal properties (Stefan, 1891). An infinite slab was divided into two regions, the crust and core, and macroscopic balances were used to develop the governing partial differential equations for heat and mass transfer in each region. Farkas et al. (1996) are perhaps the first ones to include pressure-driven flow, although restricting such flow to the crust region and for vapor phase only. Ignoring vapor flux in the core and liquid flux in the crust reduced mathematical complications. The oil phase and the changing porosity were not included on their model. The use of a constant diffusivity limits the model as it should be a function of temperature, moisture content, physical structure, and position. Other moving boundary models have been reported (Bouchon and Pyle, 2005; Farid and Chen, 1998), however most were solving only the heat transfer equation and no mass transport have been considered

A multiphase (water, oil, vapor, air, solid) porous media model that consider a distributed evaporation region within the media rather than only a sharp boundary

formulation has been presented for the first time by Ni and Datta (1999b). According to the authors, in a given situation, it is possible that the real evaporation zone is very narrow, similar to the sharp interface and distributed evaporation formulation. This mechanistic model was able to predict such narrow evaporation zone. At high rates of internal evaporation, significant pressure driven flows can be present for all phases and throughout the material. In their model, all the significant transport mechanisms (molecular diffusion, capillary, and pressure driven flow) and all the phases kept their individual identity. Uptake of oil during frying was implemented as a diffusion term by Ni et al. (1999) with a constant oil concentration boundary condition, which in reality it is not constant, also the cooling stage was not included. Application of the distributed evaporation formulation in a multiphase porous media to describe multiple processes has shown its versatility. A wide range of heating modes and processing situations are cited on the literature: microwave heating (Ni, 1997), baking (Ni and Datta, 1999a), frying (Ni and Datta, 1999b; Yamsaengsung and Moreira, 2002b).

Up to this point, few models (Ni and Datta, 1999b; Yamsaengsung and Moreira, 2002a) have implemented the local equilibrium approach for description of water evaporation, where water in the solid matrix is assumed to be in equilibrium with water-vapor in the surrounding. However, it has been demonstrated for pure water that this does not hold true (Ward and Fang, 1999). In 2007, Halder et al. (2007) used for the first time a non-equilibrium approach for evaporation in their deep-fat frying modeling. This new approach allowed a more generalized description of the physics and also this new formulation facilitated its implementation on a typical CFD (computer fluid dynamics)

software. It could explicitly express the evaporation rate in terms of concentration of vapor and temperature. In an equilibrium formulation, the evaporation is an implicit variable which cannot be implemented in any direct manner in the framework of most commercial software.

One of the major limitations of these multiphase porous media formulations (Bouchon and Pyle, 2005; Halder et al., 2007; Halder et al., 2010; Ni et al., 1999) is the complete disregard for geometry changes. Instead, an equivalent porosity is defined as the fraction of the total volume occupied by liquid water, oil, water-vapor and air. To calculate the concentration of each phase, the equivalent porosity value is used, which is assumed to be constant during the frying process. The gas porosity is used to approach the effect of structure change. As the product loses water, the gas porosity increases and so does its intrinsic permeability.

Yamsaengsung and Moreira (2002b) took in consideration structural changes during deep fat frying of tortilla chips on their mechanistic model, which also used a distributed evaporation formulation. Semi-empirical correlations were included on the model to account for the structural changes such as shrinkage and expansion of the product. However, they did not consider post-frying cooling process as a continuation of the frying process where the initial conditions for post-frying cooling should be the end condition of the frying process. They inputted separate initial conditions for frying and cooling.

Few studies have been done on modeling of heat and mass transfer for frying processes on the last decade, but most notably, only very few studies have been found under the light of transport phenomena for frying processes under vacuum atmosphere.

Yamsaengsung et al. (2008) proposed another model for vacuum frying of potato chips where the rate of moisture loss was separated by two parts, the constant rate and the falling rate period of drying. Two sets of diffusion coefficients were used for oil and water (one for the falling and another one for constant rate period) in the mass transfer equations.

Troncoso and Pedreschi (2009) used two models based on the Fick's law to describe water loss of pre-treated potatoes slices fried under vacuum. The first model includes a constant effective diffusive coefficient, and the second uses a variable effective diffusive coefficient. The variable diffusivity model fitted best the experimental water loss data. It was assumed that the variable diffusive coefficient accounted for probable changes in physical properties of the product during frying. For the oil uptake, the data were fitted to an empirical model, with a linear behavior for short times whereas the model was time independent for longer times. The simulation also showed the crust formation and its gradual movement inward, thus a moving boundary approach was considered as well. This was the same approach used by Farkas et al. (1996) for atmospheric frying, a complex form of the Stefan class of problem. This model predicted a rapid flux of oil into the product during the constant drying stage, followed by a small amount of oil absorption into its interior once the crust was formed.

Warning et al. (2012) used the multiphase porous media approach to model heat and mass transfer within a potato chip fried under vacuum using commercial CFD program for its implementation. A discrepancy between predicted and experimental oil content during the initial stages of frying can be observed. There is a lag in oil absorption in experimental data compared to the predict one. The formulation of oil diffusivity could possibly explain this discrepancy. The oil permeability and diffusivity in the model were unable to capture the effect of changing pore size and other physical changes in the potato chip during crust formation. Collapsing and expanding pores, along with gelatinization of the potato starch greatly affects permeability. Also, this study disregards the depressurization and pressurization stages of vacuum frying. Oil absorption is highly dependent on the pressurization stage at the end of frying, are reformulation of these boundaries' conditions are needed to capture all the fundamentals of mass and energy transport for the oil phase.

Sandhu and Takhar (2018) used a two-scale hybrid mixture theory (HMT) based unsaturated transport equations developed by Takhar (2014) to predict moisture and oil content, evaporation rates, temperature distribution, and pore and gas pressure profiles as a function of frying time and temperature of potato discs fried at atmospheric pressure. This approach takes into account the thermo-mechanical changes in the porous matrix of the potato disc, which have not been considered in the previous modeling studies. In a previous HMT based frying study, not published, the model predicted moisture content and temperature accurately according to the authors, however experimental data resulted in higher oil content due to penetration of surface oil during cooling stage, which is not

taken in account here. Therefore, in the current study, a different approach was used in which the model validation was performed by making comparison between predicted and experimental oil content values after removing the surface oil, which was expected to have penetrated during post-process cooling. Thus, the cooling phase is not accounted in this model either. Percentage average absolute difference between predicted and experimental values for oil content during frying was 14%, 31% and 20% at 150,170 and 190 °C, respectively. The authors claimed that this level of accuracy was expected for oil uptake prediction, as the transport properties of oil (diffusivity and permeability) and other properties such as capillary pressure are not known precisely in function of those frying temperatures. They emphasize that further research into development of techniques that measure the material properties and oil content more accurately at frying temperatures is expected to improve the accuracy of the model.

Naghavi et al. (2018) developed a 3D model to simulate momentum, heat and mass transfer during atmospheric deep-fat frying of uncoated or coated potato strips. The effects of different concentrations of sodium alginate and four different locations of potatoes in fryer on moisture content (MC), oil uptake (OU), core (T_{co}) and surface (T_{surf}) temperatures of the samples, oil temperature (T_o), and oil velocity ($\vec{u}_o$) were investigated. Some compromises on the physics of the formulation are also found here: shrinkage and volume change were considered negligible for the solid phase; most of the physical properties such as density, thermal conductivity, and specific heat of the components were considered constant throughout the process, although different properties were assigned for the core and for the crust; multiphase effects were not considered. It was

assumed that vapor flows in the solid and from sample's surfaces into oil, while no liquid water is allowed to flow into oil phase. It was assumed that the value of water vapor diffusivity of potato strip is the same as water vapor diffusivity in frying oil. The results of numerical modeling showed underestimation of the *OU*. The discrepancy (*E%*) between modeling results and experimental data for oil uptake was in the range $18.86\% < E\% < 26.87\%$. This was mainly attributed to the fact that the effects of *oil uptake* mechanisms during the cooling period or drainage (such as capillary pressure-driven mechanism) on the total *OU* of fried samples were not considered in this simulation.

Summarizing, several models with various levels of complexities have been proposed to explain the mass and heat transfer phenomena in deep-fat frying processes. Some assuming constant properties throughout the process, some adopted simple diffusion formulations for energy and mass transfer, some accounted for evaporation, others did not include the oil phase transport during the cooling stage, and most not even accounted for physical structure changes. Modeling of these mass and energy transport phenomena in frying, where time and size scales are so small, has come a long way. However, there is a need for information of parameters and properties of materials that could make modeling on those systems more accurate.

3.7. Vacuum frying – alternative for new products

In the last decade, a variety of studies using different sources of raw materials for vacuum frying have been published. Different aspects of this technology were observed in those studies.

In an optimization study for vacuum fried processing, plantain chips had shown higher acceptability on sensory properties than atmospheric fried samples (Olayina Righteous et al., 2014). The effect of vacuum frying and structural changes in bananas (Yamsaengsung et al., 2011) and the use of edible coatings and post-frying centrifuge step on quality of vacuum-fried banana chips were also investigated (Sothornvit, 2011).

Studies on mango had shown higher carotenoid retention, brighter yellow color, crispier texture, and lower oil content on vacuum fried products when compared to atmospheric fried ones (Da Silva and Moreira, 2008; Nunes and Moreira, 2009; Villamizar et al., 2012).

The effect of different low pressures on the moisture diffusivity of apple chips was analyzed by Bravo et al. (2011). It was observed that, at a given temperature, the diffusion coefficient increased as the pressure decreased. This increase has been described as a potential function. The close fit obtained between the moisture loss model and heat transfer can be used to establish the desirable frying conditions as a function of the pressure.

Mariscal and Bouchon (2008) compared atmospheric and vacuum frying of apple slices in terms of oil uptake, moisture loss, and color development. To carry out appropriate comparisons between both technologies, they used an equivalent thermal

driving forces for both processes (ΔT = 40, 50, 60 ºC), keeping a constant difference between the oil temperature and the boiling point of water at the working pressure. When the products were dried prior to vacuum frying, fried slices absorbed less than 50% of the oil absorbed by atmospheric fried ones.

The effects of pretreatment and processing conditions on the quality of vacuum fried apple chips were also studied by Shyu and Hwang (2001). The results showed that moisture content, oil content, color, and breaking force of apple chips were significantly ($p < 0.05$) correlated with concentration of immersing sugar solution, frying temperature and frying time. The optimum conditions for the process were a vacuum frying temperature of 100–110°C, vacuum frying time of 20–25 min, and immersing fructose concentration of 30–40%.

Quality parameters of vacuum (1.92 inHg) and atmospheric fried carrot, potato, and apple slices to determine specific advantages of vacuum technology was also investigated by Dueik and Bouchon (2011b). Slices were fried using equivalent thermal driving forces (ΔT = 60 and 80 °C), resulting in frying temperatures of 160 and 180°C, and 98 and 118°C, for atmospheric and vacuum frying, respectively. Vacuum-fried carrot and potato chips absorbed 50% less oil than atmospheric-fried chips, whereas vacuum-fried apple chips reduced oil absorption by only 25%. They showed that total carotenoids and ascorbic acid (AA) were greatly preserved during vacuum frying. Carrot chips vacuum fried at 98 °C retained about 90% of total carotenoids, whereas potato and apple slices vacuum fried at 98 °C, preserved around 95% of their initial AA content.

Response surface methodology was used to investigate the effects of higher levels of maltodextrin (40-70%) as a pretreatment for gold kiwifruit slices and temperature/time used during vacuum frying of the samples on the moisture, oil and ascorbic acid contents of the products (Diamante et al., 2011a). Moisture content of vacuum-fried decreased with increased frying temperature; oil content of the sample increased with increased frying temperature and time. Ascorbic acid content of the sample decreased with increased frying temperature and maltodextrin level. They concluded that the best operating conditions for vacuum-fried gold kiwifruit slices are temperatures of 72.0–76.3ºC, frying times of 35.0–65.0 min., and maltodextrin level of 40% to achieve a product with moisture contents of 8.4–8.9% (dry basis) and acceptable qualities.

The effects of maturity, pre-treatment, and processing on the physiochemical content and sensory attributes of jackfruit were assessed by Diamante (2008). They showed that vacuum fried products from ripe jackfruit had significantly higher moisture content (55-57%), higher oil content, and higher yield than the products from half-ripe jackfruit. Blanched and frozen ripe and half-ripe samples had significantly higher fat content than the products from fresh ripe and half-ripe samples. The color, texture, and oiliness acceptability of the vacuum products from half-ripe samples showed that these products were significantly better than the products from ripe samples. While the aroma, sweetness, and general acceptability of vacuum products from ripe samples were significantly better than the products from half-ripe samples.

A preliminary investigation of the effect of pre-treatments on sensory characteristics of vacuum fried pineapple snack can be found in the study of Hasimah et al. (2011). Different pre-treatments were carried out on pineapple *Ananas comosus* 'Moris' to explore the effect of blanching, syruping, and freezing on the fried snack produced by vacuum frying. Pineapple snacks produced by blanching, followed by syruping, and freezing were much better in appearance and texture as compared to snacks produced without any treatment, blanching alone or a combination of blanching and syruping pre-treatments.

The effect of vacuum frying on the physiochemical and nutritional quality parameters of pineapple chips were also investigated by Perez-Tinoco et al. (2008). Slices of MD-2 pineapple hybrid were vacuum fried at 24 kPa for different frying times (6.3-7.7 min) and temperatures (106.3-117.7°C). Moisture content, water activity a_w, color parameter, and total vitamin C content decreased while total phenolic content and dehydroascorbic acid content increased with increasing frying time and temperature. It was determined that processing conditions of 6.9 min frying time and 112ºC frying temperature produced pineapple chips with a golden color, an a_w of less than 0.29, a moisture content of about 4%, and a crispy texture. Oil content was about 20% (d.b) and residual total vitamin C content of 90 mg/100 g wet basis (w.b.). Phenolic compound content was about 150 mg gallic acid /100 g w.b. and antioxidant capacity was around 22 μmol Trolox /g (w.b.). The authors concluded that vacuum frying was an effective process to produce healthy fruit snacks which partially preserve the fruit's original color and nutritional compounds, preserving the product's hydrophilic antioxidant capacity.

3.8. New approaches

Innovative approaches in processing and technology are being developed aiming to mitigate several challenges such as oil absorption reduction, processing time reduction, and development of new products.

Vacuum frying is the most versatile technology to produce new fried snack products. Since it employs considerably lower temperature ranges (100-140ºC) for frying, it allows the use of several fruits and vegetables as raw materials without the detriment of color and nutritional components, which is cause by higher scorching-temperature ranges. Examples of accentuation of color and retention of nutritional attributes of several fruits and vegetables can be found on the study done by Da Silva and Moreira (2008). The enrichment of thermo-sensitive bioactive components such as phenolics from beetroot in raw products like potatoes have been possible by the use of vacuum frying (Moreira and Almohaimeed, 2018). Although vacuum frying not always speed up the dehydration process, it significantly keeps the oxidative stability of the frying oils for longer when compared to conventional frying since it is mostly carried out on a deprived oxygen environment (Crosa et al., 2014).

Another processing technique used in vacuum frying is the two-stage (TS) frying process. It involves the product to be fried at a short period of time in atmospheric pressure (first stage) and then under vacuum conditions for the remaining of the processing until product doneness is achieved. Ravli et al. (2013) fried sweet potatoes in a two-stage frying process (1 min fried at atmospheric pressure and 2 min under vacuum) and showed that the final product had better appearance and texture compared

to the ones that were only fried under vacuum or single-stage (SS) conditions. The TS samples were lighter and more yellow (less compact) than the chips fried under the SS process. The atmospheric frying prior to vacuum frying helped the surface starch to gelatinize, restricting steam escape, which would lead to product volume expansion during the vacuum stage until the structure settles at the end of frying. It resulted on a lower bulk density product, more porous, producing a better product in terms of texture, oil content, and flavor. The final oil content of the TS fried chips was 15% lower than those fried by the SS process showing that the structure of the chips formed during the process affected the oil absorption during frying.

A recent trend is the concept of hybrid/combination mode or otherwise called microwave-assisted food processing technologies, which utilizes microwave to enhance conventional or nonconventional food processes, consequently obtaining high end products that is not readily achievable by traditional techniques (Kim et al., 2012). One of the main aspects that this technology overcomes, compared to other conventional methods, is the processing time reduction. Microwaves are a form of electromagnetic radiation in frequency ranging from 0.3 GHz to 300 GHz with wavelengths from 1 mm to 1 m. Microwaves interacts with polar water molecules and charged ions, generating frictional heat from molecular alignment and migration of charged ions in rapidly alternating electromagnetic field. Microwaves are currently being used in both domestic and industrial scale for various applications like cooking, baking, drying, thawing, and more recently, frying (Pankaj and Keener, 2017).

Parikh and Takhar (2016) compared the real-time pressure and temperature profiles of French fries fried under microwave (MF) and conventional frying (CF). Microwave frying showed greater magnitudes for the gage pressure and lasted longer, and the temperature increased to boiling point of water faster in comparison to conventional frying. Lower magnitude of negative pressure during microwave frying was the reason to have caused lower fat content in fries obtained in the microwave frying process. Micro-Computer Tomography images showed a crust with compact structure was formed due to moisture loss in CF sample. The authors hypothesized that the crust was expected to resist the escape of moisture and expansion of vapors in the core of the French fry. The expanding vapors in the core caused merger of smaller pores by rupturing the solid walls surrounding them. The rupture of solid walls caused larger pores in the core of the French fry. Conversely, for MF, since the moisture evaporation was uniform throughout the French fry, the crust was less compact than the CF sample's crust, which was expected to have caused easier escape of moisture and vapors. The lesser resistance posed by the crust was expected to have caused less merger of smaller pores in core. The microwave technology still faces the challenges to produce a uniform field for its application. Non-uniform heating and deterioration of oil at high temperatures are the main disadvantages. Aydinkaptan et al. (2016) have shown that power level was an important factor in terms of oil degradation during repetitive microwave heating frying. They showed that microwave heating resulted in higher values of investigated oil oxidation-parameters (free fatty acid, peroxide values, total polar material, viscosity, refractive index, redness and yellowness) relative to the

conventional method throughout heating and lower values of linoleic acid content at the end of heating period. This could limit the use of microwave frying as a standalone technology.

Currently, some researchers are seeking to combine microwave heating technology with vacuum frying to reduce such oxidation problems and be able to produce better quality products in less time while reducing oil absorption (Quan et al., 2014; Song et al., 2007; Su et al., 2016). Su et al. (2016) compared potato chips produced using microwave vacuum frying (MVF) and vacuum frying (VF) technologies. Results have shown that the moisture evaporation rates were accelerated and the MVF produced crispier chips with better natural color. Higher microwave power densities resulted in faster water evaporation rates and lower breaking force. Higher frying temperature led to faster water evaporation, lower oil content and faster color change. Higher vacuum degree brought faster water evaporation, lower oil content and less color change. A comparison of scanning electron micrographs of MVF and VF samples shows that the cellular structure and integrity of cell wall of samples were better preserved by MVF than VF Although microwave-assisted vacuum frying has helped to increase water evaporation rates and produce lower oil content products, there has not been any work in the scientific literature showing its effect on the oil oxidation stability. This has been one of the proposed advantages of the use of a low oxygen frying atmosphere to offset the issues of oil oxidation reported by the use of microwave heating.

Another approach to decrease frying temperature in MVF systems has been studied through the incorporation of ultrasound waves. An ultrasonic microwave-

assisted vacuum frying (USMVF) has been designed and tested by Ya et al. (2018) as a novel frying technique for potato chips at lower frying temperature ranges. USMVF experiments were carried out by a combination of ultrasound and microwave power settings in a vacuum frying system for potato samples at two frying temperatures, 90ºC and 100ºC, and compared to microwave-assisted vacuum frying (MVF) at the same temperatures. Based on the analysis of drying kinetics and quality assessment, the USMVF markedly increased the moisture evaporation kinetics and effective moisture diffusivity, reducing 20-28% of the drying time compared with the MVF, especially at lower frying temperature. The oil uptake of fried potato chips was reduced (21.4%) in the USMVF. Texture property (crispness) and color of fried potato chips were improved by the combination of ultrasound in MVF. A more porous microstructure in USMVF samples was observed by SEM. Although this work showed better results for the ultrasound-assisted MVF process, it might not show a fair comparison since MVF uses higher temperatures for processing (100ºC to 150 ºC). However, oil oxidation could have been reduced due to the use of even lower temperature ranges in USMVF.

In a different study, Su et al. (2018) compared USMVF processing at various ultrasound and microwave power settings to vacuum frying (VF) processing of purple-flesh potatoes. Both processes were carried out at 90ºC of temperature, and 10 kPa of pressure. The USMVF resulted in higher moisture evaporation rate and effective moisture diffusivity compared to the VF process. The oil uptake was reduced by 16–34%, shrinkage was lowered, and the texture (crispness) and the color of fried samples were improved in the USMVF process. The same explanation regarding a fair

comparison must be made here, since VF processes usually operates in the 120-140ºC range. However, as pointed out, oxidation levels of oil or preservation of thermo-sensitive compounds could have been improved due to the lower temperature range used in USMVF. In this work, the authors found that the total anthocyanin levels and retention of fried purple-fleshed potato chips fried in the USMVF system achieved the highest levels (123.52 mg/100 g solids and 79.51% retention, respectively). SEM analysis revealed a more porous microstructure in USMVF samples. It has to be noted that a centrifuge was used to remove the surface oil of products after deep-fat frying at a high rotational speed (370 rpm). It does not say the dimensions of the centrifuge; therefore, it is difficult to make a fair comparison with other works since centrifuge forces cannot be calculated. A vacuum breaking switch was turned on after the de-oiling process to maintain consistent speed of air current in every frying process.

Radiant heating for food processing has been around for a few decades. It was used in several cooking processing, such as infrared drying, infrared cooking, infrared baking and radiant frying (Pankaj and Keener, 2017). Many devices were patented. They would rely on a constant heat flux from an emission source to maintain a set point temperature of the product's environment. When used alone, constant flux heating would produce foods with a charred surface and under-heated core unless microwaves were also used for proper wave penetration.

Farkas and Hubbard (2000) hypothesized that the unique and desirable properties of fried foods were a direct result of the dynamic nature of the heat flux found in immersion frying. The rapid increase in flux to a peak followed by gradual decrease

results in the setting of a porous matrix (crust) with continued internal heating without burning. This had led the development of a technology that could overcome those limitations. The concept of controlled dynamic radiant (CDR) process to mimic immersion-frying processing was developed. The effect of finish heating method (oven heating, immersion frying and controlled dynamic radiant (CDR) heating) on mechanical properties, color and sensory properties of parfried French fries was first evaluated by Lloyd et al. (2005). Peak breaking force was highest for CDR-heated French fries. An equivalent "b" value (yellowness) for the crust of immersion fried and CDR-heated French fries was found by using color analysis. Sensory evaluation indicated overall acceptability of CDR-heated French fries equivalent to immersion fried-French fried potatoes. Finish heating of par-fried French fries using CDR heating showed promise to produce a reduced-fat fried product, as well as an alternative process to traditional immersion finish frying. More recently, Melito and Farkas (2012) showed that all CDR-finished donuts had significantly ($p \leq 0.05$) lower fat content (25.6% to 30.6% d.b.) than the control (33.7% d.b.). They had comparable ($p \leq 0.05$) overall acceptance scores to the immersion fried control despite the significantly lower fat content. As an alternative frying method, CDR differs from other methods because it can mimic the heat flux generated during immersion frying for water evaporation, crust formation and browning. CDR frying uses high heat flux radiant emitters, which can produce flux rates higher than100 kW/m^2 with precise control on output to mimic the flux profile similar to immersion frying (Pankaj and Keener, 2017). A multi-zone radiant frying system have been patented for continuous CDR frying equipment by Farkas et al. (2007). Each zone

has two radiant emitters located on each side of a conveyor which are independently controlled for precise control of heat flux profile by adjusting process variables like power settings, emitter or sample geometry and product exposure time. In summary, CDR frying has shown promising results, there is a lack of recent literature on its application on food processing.

Several novel frying technologies such as vacuum frying, microwave frying, ultrasound-microwave assisted vacuum frying, and radiant frying have been discussed here. These technologies offer some advantages over the traditional methods. However, further studies are required for process variable optimization and understanding the mechanism and interaction of these technologies with different food materials.

3.9. Ultrasound - a novel technology for the food industry

To address specific consumer needs towards safe, healthy, minimally processed foods, the development of emerging technologies in food processing was necessary. Nowadays, ultrasound, high hydrostatic pressure, pulsed electric fields, and cold plasma have found applications in the food industry and related fields. The use of specific potentials and applications of each of these new processes opens a wide field of opportunities to understand the complex relationship of food-structure, functionality, and process control.

Significant science-based achievements have been made to better understand the basic principles underlying the ultrasound process, however its application in food industry has seen limited efforts (Yanniotis et al., 2013).

Several studies have reported successfully application of ultrasound technology to assist with food preservation, texture changes, analysis, and thermal treatments. In this particular study, the sonication process (use of ultrasound waves for processing) was applied to improve mass transfer on pre-treatments of raw potatoes prior to conventional deep-fat frying.

3.9.1 Ultrasound - physics

Ultrasound has been used in a wide variety of applications nowadays. The development of sonars, non-destructive tests, biomedical imaging has produced an abundance of literature since the beginning of the First World War, where its potential as a viable means to detect submerged object became apparent. But prior to that, the use of ultrasound in medicine had initially begun with rudimentary applications in therapy, such as tissue breakdown, rather than imaging. This destructive ability of high intensity ultrasound was observed by a wartime scientist, Langevin, when he noted the death of schools of fish in the sea and pain induced in the hand when placed in a water tank insonated with high intensity ultrasound. It was around this time that development work into the use of high intensity ultrasound for industrial processes began (Harvey et al., 2014).

In this study, the focus was on ultrasound waves, where it can be called “high intensity or power” ultrasound. This type of ultrasonic field should directly influence a process, causing some type of physical change on an object through the exposure of such high vibrational energy field. Usually those changes are caused by the induction of cavitation within the target object or field. In order to efficiently generate cavitation,

these high-power applications operate using rather low frequencies (10 kHz to 1000 MHz).

Acoustic cavitation is the basis of many applications of ultrasound in this frequency range. It is simply the induced bubble activity within a fluid under an ultrasonic field. Bubble activity can be merely the oscillation in radius size caused by an incident sound wave, however the desired effect depending on the application, might not be achieved if certain parameters are not met. In a fluid under an ultrasonic field, the expansion of microscopic bubbles might be expected during the negative cycle of the propagating wave. The pressure fluctuations within a fluid under ultrasonic field might induce the formation, growth and fragmentation of microbubbles within that fluid. The event of a collapsing bubble is a microscopic implosion that generates high local shear and the release of heat energy. If the amplitude of the acoustic waves is sufficient, these bubbles will undergo several rapid expansions before reaching a critical radius, R_{max}, at which point the bubble suffers a violent collapse (Apfel, 1981), where R_{max} is defined as shown in Equation 3.1. This is referred to as the "cavitation threshold" (Peregrine, 1994), which defines the acoustic intensity which must be exceeded in order for cavitation to be supported and is a function of the operational frequency for the acoustic source, the hydrostatic pressure and the viscosity of the medium. Equation 3.2, describes the bubble behavior prior to collapsing, it is known as the Rayleigh-Plesset equation. This equation and its variations can be used to estimate the cavitation threshold for dynamic transient cavitation.

$$R_{Max} = 2.3R_o \tag{3.1}$$

Where R_0 = bubble equilibrium radius.

$$R\ddot{R} + \frac{3\dot{R}^2}{2} = \frac{1}{\rho}\left[\left(p_o + \frac{2\sigma}{R_o} - p_v\right)\left(\frac{R_o}{R}\right)^{3k} + p_v - \frac{2\sigma}{R} - \frac{4\eta\dot{R}}{R} - p_o - P(t)\right] \tag{3.2}$$

Where R = instantaneous bubble radius, $P(t)$ = dynamic pressure, σ = surface tension, ρ = medium density, p_v = vapor pressure, p_0 = hydrostatic pressure, κ = polytropic index and η = sheer viscosity.

Within the region of collapse, several spectacular effects are likely to occur, including an internal bubble temperature of 3000 ºK and pressure shockwave emission reaching 6 GPa (Pecha and Gompf, 2000). This type of behavior or bubble motion is called transient cavitation, or simply inertial cavitation. This entire cycle can occur several times to the seed bubble before it fragments, all in a matter of microseconds. If inertial cavitation is not induced, it happens when the amplitude of the acoustic wave is below the threshold, the alternative motion of the bubble is referred to as stable or non-inertial cavitation. Compared to transient or inertial cavitation, non-inertial cavitation is stable, non-destructive and long lived. Figure 3.4 shows the possible several states for a seed bubble excited by an ultrasonic field.

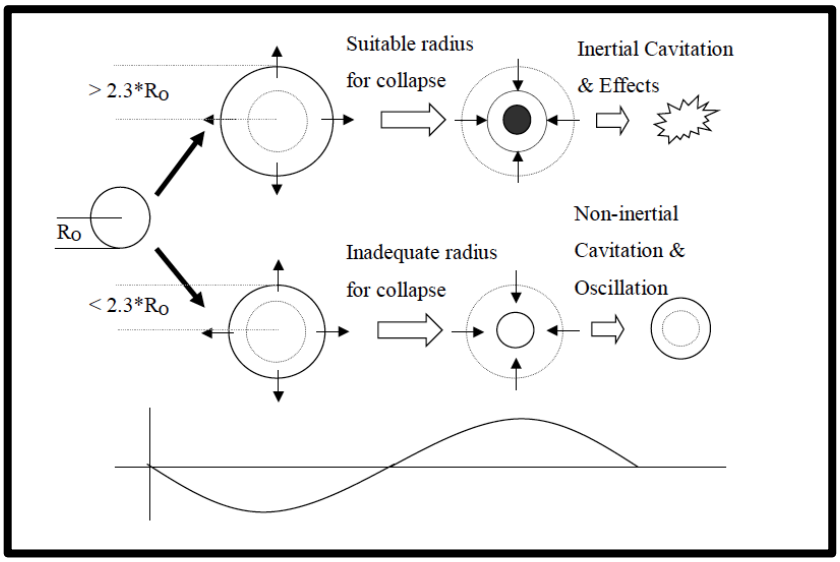


Figure 3. 4. A typical seed bubble being excited by an acoustic wave - Reprinted from Harvey et al. (2014).

The bottom path demonstrates bubble behavior when acoustic amplitude is relatively low: non-inertial cavitation. The top path when acoustic amplitude is great enough to cause the bubble to expand past R_{MAX}: inertial cavitation.

Several applications can be utilized using these effects. Spotty heat emission due to the collapse of the bubbles can induce the formation of free radicals, also the local temperature increase can improve chemical reaction rates of some processes. High shear due to pressure fluctuations from shockwave emissions can lead to mechanical effects such as mixing and shearing, which can optimize contact between reactants, or even accelerate dissolution or aid the renewal at the surface of a solid reactant (Leong et al., 2011).

3.9.2 Ultrasound waves - production

A system for producing ultrasonic waves consists of three main different parts: the generator, the transducer and the application system. The generator is the source of energy. In fact, all methods used for producing ultrasonic fields convert another kind of energy (electric, magnetic, kinetic) into acoustic energy. The transducer is responsible to carry out this conversion. According to the phenomena involved three main types of transducers could be considered: fluid-driven, magneto strictive and piezoelectric. The fluid-driven transducer produces an acoustic wave when the kinetic energy of a fluid makes a mobile part of a system vibrate. The magneto strictive transducer is made from a kind of material that changes in dimension upon the application of a magnetic field. If the magnetic field disappears, the material returns to its original shape. Repeated changes of shape produce the sought-after mechanical vibrations. The piezoelectric transducers produce acoustic energy by changes in size produced by electrical signals in piezoceramic materials. The piezoelectric transducers are the most common devices employed for the generation of ultrasound. The mostly widely-used equipment in research include sirens and whistles (the air application is generally in human audible range that could be an obstacle to its use (Mulet et al., 2003), stepped-plate transducers, ultrasonic baths, and probe systems. Among those, the ultrasonic bath is the ultrasound source for most experimental results published in the literature (Mason, 1998). This kind of equipment consists of a metallic carcass with piezoelectric transducers attached to the bottom. When transducers vibrate, they transmit their vibration to the whole carcass, then the carcass transmits the vibration to the liquid. A problem in obtaining consistent

results lies in the reflections on the air–liquid interfaces that produce standing waves and an irregular ultrasonic field inside the bath (Mulet et al., 2002).

In this study, an ultrasonic bath system was used, usually known as ultrasonic cleaner. The majority of high intensity applications function at relatively low frequencies, and ultrasonic cleaning are very common for this type of use. Operational frequencies generally range from 20 to 50 kHz depending on the task. For example, a 25 kHz cleaner will have more cleaning prowess than a 50 kHz cleaner since the likelihood of cavitational effects is higher at lower frequencies. However, lower frequencies can prove damaging to delicate parts hence 50 kHz and above may be preferable for some applications, i.e. the semiconductor industry. In terms of health and safety for operators, higher frequency cleaners are also quieter due to the lack of energy in the audible range (Harvey et al., 2014; Mason and Peters, 2002).

3.9.3 Measurement methods

Measurement methods for these high-power fields are important for safety and process efficiency reasons yet, currently, there are very few well-documented and reliable measurement methods available. They can be extremely difficult to characterize, often due to the cavitational activities themselves. Not only can cavitational effects cause damage to any measurement instrumentation being used, but regions of dense bubble populations can also scatter the source acoustical signal under investigation. This often facilitates measurements being obtained under non-cavitational conditions. Nevertheless, conducting measurements in non-cavitating fields may not yield true pressure distribution experienced during a high-power application, but it can identify locations

where cavitational sites are likely to occur when sufficient power levels are reached. Traditionally, hydrophones are the principal device for field characterization in many applications with use in medical ultrasound for exposure quantification widely reported. There are a number of important factors to consider in hydrophone design whether it is piezoelectric ceramic based or, more recently, piezoelectric polyvinylidene fluoride (PVDF) membrane. The device itself should be non-perturbing to the acoustic field in order to minimize any detrimental effect on the field profile, although the physical nature of the probe makes complete non-invasive measurement impossible in reverberant environments. Furthermore, many hydrophones suffer from a lack of uniform response over a wide range of frequencies while still maintaining sensitivity, particularly below 200 kHz where the majority of high-power applications operate. In addition, any measurement probe must be robust enough to withstand the hostile fields associated with high power ultrasound measurement (Harvey et al., 2014).

Common measurement methods include broadband acoustic emission, aluminum foil erosion, chemical effect monitoring (chemiluminescence) and sonoluminescence (Carnelli et al., 2012; Hodnett and Zeqiri, 1997). Despite the attractiveness of these two luminescence techniques and their potential for high spatial resolution, the requirement for blackout conditions in optically transparent media renders them complex to implement in practice. Conversely, passive acoustic methods incur none of the complications associated with the optical techniques and, consequently, are more widely applicable. Potassium iodide dosimetry has been another method used to measure the intensity through the oxidation of iodide ions to iodine where they then form a chemical

complex with excess iodine to form tri-iodide (Morison and Hutchinson, 2008). Another summary of radical formation through an ultrasound field and its determination can be found in (Leong et al., 2011). While chemical experiments have their limitations, they have been shown to give results which correlate closely with those obtained from acoustic emission measurements (Zeqiri et al., 2003).

In summary, in most of the studies found in the literature, the ultrasonic intensity and frequency are the main parameters considered in ultrasound application (Cárcel et al., 2007). Some authors take into account the existence of a relationship between ultrasonic intensity and the appearance and magnitude of ultrasound effects (Lenart and Ausländer, 1980). Nevertheless, the effect of intensity is seldom addressed. On the other hand, the ultrasonic frequency used in high intensity ultrasound applications is usually around 20 kHz, as higher frequencies result in an increase of energy absorption by the medium and, as a consequence, the remaining energy at the interface and in the food-material to be treated, is significantly reduced. The ultrasound intensity applied to the medium is generally reported either as the electrical consumption of the generator or as the electrical energy supplied by the generator to the transducer (Raso et al., 1999). However, this approach does not provide complete information about the ultrasonic field applied since it also depends on other parameters such as size and geometry of the treatment vessel, characteristics of the medium (e.g. viscosity, surface tension, vapor pressure, concentration, temperature, impedance matching (Mason and Lorimer, 2004). Therefore, the electrical/acoustic energy conversion factor determines the amount of acoustic energy applied (Lin and Zhang, 2000). To determine the influence of ultrasound

intensity in a process and to be able to compare different treatments, it is necessary to measure the actual ultrasonic energy transferred to the medium. Different methods have been developed for measuring acoustic fields, among which, the use of microphones/hydrophones and the calorimetric techniques (cited above) are some of the simplest and most reliable.

3.9.4 Application of ultrasound in the food industry

The use of ultrasound in the food industry can be noted in many areas such as packaging, particle size control, imaging process coupled with tomography, material properties, monitoring shelf life and preservation. These applications belong more in the diagnostic spectrum rather than of processing. High power ultrasound is becoming a reliable tool to favorably change products physical properties, enhance mass transfer, as they undergo processing. The increase demand from consumers to obtain more nutritional products and safer to be consumed, has pushed the industry to seek for other technologies to achieve this demand. The used of ultrasound has shown to be an effective tool in several of these applications in the food industry (Ahmed et al., 2016; Bermudez-Aguirre, 2017; Mulet et al., 2003).

Some researchers also have used power ultrasound together with thermal processing and chemical techniques to reduce microorganism loads (Piyasena et al., 2003).

Many other valuable uses of ultrasound (from hereafter this manuscript will mean “power ultrasound”) in the food processing include: enhancement of fluid extraction from vegetable tissues, sterilization, improvement of crystallization quality in

freezing processes, meat products tenderization, change in viscosity of starchy materials through depolymerization, in biotechnology through modification of enzyme and cell activities, and glucose release from corn in ethanol plants (Chandrapala et al., 2012; Iida et al., 2008; Jiménez-Sánchez et al., 2017a, 2017b; Khanal et al., 2007; Kiani and Sun, 2011; Mason, 1998; Mason, 2007; Saclier et al., 2010; Yu et al., 2012).

3.10. Mass transfer enhanced by ultrasound

Many mechanisms are attributed to enhanced mass transfer in several unit operations in the food industry (drying, osmotic dehydration, hydration, and salting) through the use of ultrasound waves in the scientific literature, many of which are cited in (Miano et al., 2017). Microchannel formation, acoustic cavitation, inertial flow, microstreaming, and microjets are among the most cited in the literature for the processes mentioned above. Some of them are attributed to be the dominant phenomena taking place in some specific unit operations, and sometimes a combination of those are credited to be the determining variables for the mass transfer. Despite of all those affirmations, demonstration of such mechanisms is rarely seen in the scientific literature.

It is very well known that mass transfer processes are a function of two types of resistances, internal and external. Figure 3.5 shows the main mechanisms that govern the mass transfer enhancement by ultrasound in a food material.

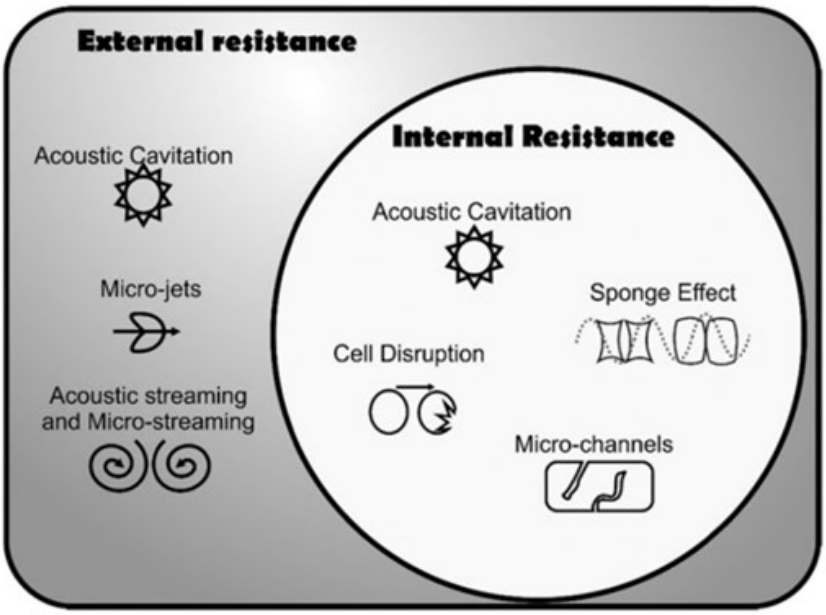


Figure 3. 5. Main mechanisms of mass transfer enhancement by ultrasound in food material – Reprinted from Miano et al. (2017).

3.10.1 External resistance to mass transfer

External resistance to mass transfer is found in the bulk fluid that surrounds the food material. Convection of the fluid is responsible to transfer mass by the bulk fluid motion, agitation is used to increase the convection of the fluid, therefore decreasing resistance for this type of mass transfer. Ultrasonic waves can induce agitation of that fluid on those interfaces (fluid and food material) as well, by inducing acoustic streaming (oscillatory motion of the fluid). Microstreaming is formed when the ultrasonic wave propagation reaches boundaries (food surfaces, microbubble surfaces, wall container), generating microturbulence. Microstreaming can also improve mass diffusion in the bulk flow. Acoustic cavitation in the fluid can also form microjets when the microbubbles implode. Asymmetric collapse of the microbubbles is the main cause

for microjet formation, which in turn causes erosion of food surfaces, thus increasing the superficial area and therefore reducing the external resistance to mas transfer. In the same fashion as in microstreaming, microjets can also induce bulk flow into the food material, reported in Cárcel et al. (2007) for meat brining.

3.10.2 Internal resistance to mass transfer

Inside the food material, ultrasound can enhance mass transfer through direct and indirect effects. Intrinsic factors like water activity, porosity and the glassy/rubbery state of the food material play an important role on the intensity of those effects (Cárcel et al., 2007; Miano et al., 2016a; Muralidhara et al., 1985).

3.10.2.1 Direct effects

Some effects are directly related to the ultrasonic wave as it travels through the solid medium. On the peak of the wave, a region inside the medium will be under "compression", $\Delta P > 0$, conversely, on the valley of the wave you will have an area under "rarefaction", $\Delta P < 0$. This pressure variation will cause a rapid alternating compression and expansion inside elastic food materials (rubbery state), thus causing what is called the "sponge effect", facilitating the movement of fluids inside the food material, thus reducing the internal resistance to mass transfer. Moreover, it aids unblock pores and spaces inside the food material. On rigid food materials (glassy state), this mechanism is neglected, however the pressure variation inside the pores could still cause pumping of the fluids, which is called "inertial flow" (Miano et al., 2016b). Overall, the presence of pores in the material is fundamental to enhance mass transfer through direct effect.

3.10.2.2 Indirect effects

The indirect effects are related to changes in the product structure mainly caused by the action of acoustic cavitation, which is an effect caused by the acoustic wave propagation within the food material. The implosion of the microbubbles inside the food material can cause cell disruption and increase of intercellular spaces or micro cavities/channels (Miano et al., 2016a) that might enhance fluid movement within the material, thus reducing the internal resistance to the mass transfer (Cárcel et al., 2011). Apparently, these mechanisms have a random nature, causing cells to flatten and/or lose their adhesion. These channels might appear on a disorganized manner, some contained internally within the food material, and others connecting to the outside boundary, acting like capillaries. However, not all of them will enhance mass transfer, it will depend on some variables as tortuosity, permeability, and diffusion properties. Indirect effects are directly affected by the water activity of the food material, since cavitation is directly related to the vapor pressure of the medium (Mason and Peters, 2002). Higher vapor pressures lead to higher water activities, therefore facilitating acoustic cavitation to happen. On the contrary, the presence of solutes will lower water activity, thus hindering the indirect effect since less likely acoustic cavitation will happen. Other factors that influences indirect effect are hardness and compactness of the food since cell or matrix disruption will be less likely to happen as well, therefore reducing acoustic cavitation.

CHAPTER IV

MATERIALS AND METHODS

4.1. Raw material

Potatoes (*Solanum tuberosum*) of the Snowden cultivar, were provided by CSS Farms LLC, Dalhart, Texas. Those tubers are classified as a chipping variety (dry matter greater than 20%), which provide good chipping characteristics. They were all handled on the same manner throughout this study. Stored in an environmental chamber (NATIONAL humidity chamber, Model N417532, SP Scientific, Stone Ridge, New York) with controlled atmosphere (90% relative humidity and 7ºC).

Potatoes are usually stored at lower temperatures (4-10ºC) to inhibit potato sprouting during off season. As part of their metabolism, potatoes start accumulating reducing sugars during storage, which impart sweet taste in their end products as well as making them unfit for chip processing, because of the undesirable brown color of chips and fries (Schwimmer et al., 1957). High reducing sugar concentrations are related to the browning of potato chips during frying and therefore lower concentrations result in high quality product (Mazza, 1983). The high humidity in the storage is to prevent premature dehydration of the tubers. It is well known since the experiments of Müller-Thurgau (1882) that temperatures above 10ºC change biochemical processes in the potato tuber tissue towards re-synthesis of starch from free sugars. This phenomenon is nowadays known in industrial practice as 'reconditioning' and is a necessary treatment of cold-stored potatoes, especially in those cases, where frying is one of the steps in the

processing of the potatoes. The length of reconditioning depends on the level of sugars accumulated during cold storage and on the susceptibility of different potato varieties to lose sugar during this treatment (Samotus et al., 1974). The act of reconditioning consists of subjecting potatoes to high temperature (20-22°C) for 1-5 weeks to interconvert sugars to starch and to respire off residual sugars. The application of such procedure improves recovery in the quality of potato chips (Elbashir and Saeed, 2014).

Prior to the experiments, the potatoes were reconditioned (5-10 days depending on the color they would fry) in a dark and well-ventilated place at room temperature to reduce the amount of reducing sugars (responsible to cause darkness on the fried product) prior to frying. Canola oil was acquired from local grocery stores and the same brand was used throughout all the experiments. Calcium chloride $CaCl_2.2H_2O$ (C-81 Lot 771954), laboratory grade, was from the Fisher Scientific Company.

4.2. Sample preparation

Potatoes were selected according to their specific gravity, and they ranged from 1.080 to 1.090. The selected potatoes were washed, peeled, and sliced on a mandolin (Matfer model 2000, France) to a thickness of 1.0 ± 0.5 mm (Mitutoyo Thickness Gage, Japan) and cored to a perfect round shape through a cutter of 50.8 mm internal diameter. The slices were then bathed in reverse osmosis (RO) water at 21.0 ± 1.0ºC for a few seconds to remove any residual starch from the surface and finally blotted dry with paper towel prior to any subsequent processing (pre-treatment, frying).

4.3. Sonication process

A Bransonic ultrasonic bath unit (B52 model, Branson Co., Shelton, CT), was used for all the experiments in this study. The unit consisted of a stainless-steel tank (2 gallons capacity, 9.5”x11.5” by 6.0” deep), lead zirconate titanate transducers generating acoustic waves of 47 kHz at 240W (input power unheated). A stainless-steel frame was specifically built to hold the samples at the same position for every experiment. About 16 samples (~ 34 g) in an air tight plastic bag surrounded by the pre-treatment fluid (calcium chloride solution) were submerged in the tank, which was pre-filled with ice-cold RO water (5 L). A FoodSaver™ vacuum sealer system was used to remove all the bubbles (see arrows) of air trapped inside the bag. Some of the large bubbles (see arrows) trapped in between the sample had to be manually removed with a squeegee with the care to not compress the samples (Figure 4.1).

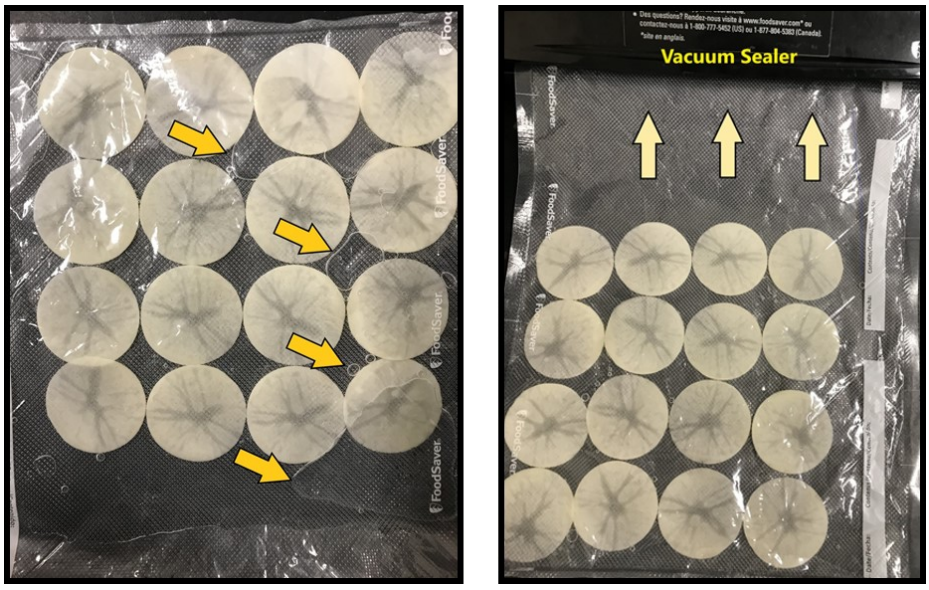


Figure 4. 1. Air bubbles (see arrows) to be removed and vacuum sealer.

The sample bag was attached using rubber bands to the custom-made frame to hold it facing flat down the bottom of the tank from a 2 inches distance (Figure 4.2). Above the bag, 3 kg of pre-made ice (RO water) was added to keep the temperature constant throughout the experiment. A small increase in temperature was noticed due to heat generated from the sonication process (0.2 ºC ± 0.2 ºC to 4.0 ºC ± 0.2 ºC). Ultrasound waves were carried through the samples continuously throughout the time of the treatment (nominal 47 KHz, 240W).

Figure 4. 2. Sample bag attachment and loading into the sonicator bath.

4.4. Preliminary pre-treatments for potato tissue stabilization

The following pre-treatment strategies were developed to evaluate their impact on oil absorption of potato chips fried at atmospheric pressure at 175°C for 55 seconds or until the final product moisture reached 2% w.b. or below.

4.4.1 Soaking

The effect of sample soaking in Ca^{+2} solutions at different concentrations and time periods was evaluated. Potato slices of 1 ± 0.05 mm thickness and 50.4 mm diameter (~ 2.125 g/slice) were submerged in calcium chloride ($CaCl_2$) solutions at concentrations of 1000, 5000, 10000, and 20000 ppm at soaking periods of 10 and 30 min. The sample to solution ratio was 6 slices (12.75 g) per 100 mL of solution. Raw potatoes without pre-treatment (soaking) were used as the control. After the soaking pre-treatment, the samples were blotted with paper towel following immediate frying. After frying, all samples were stored in Mason jars for subsequent product quality attribute tests.

4.4.2 Dehydration

The effect of alcohol dehydration and Ca^{+2} for different ratios and soaking times was evaluated. See Table 4.1 for the dehydration and Ca^{+2} pre-treatments.

Table 4. 1. Soaking times for dehydration in ethanol and Ca^{+2} impregnation pre-treatments.

Treatment	**EtOH [v/v]**	**$^{\alpha}$Soaking Time [min]**	**$CaCl_2$ [ppm]**	**$^{\beta}$Soaking Time [min]**
B-1 (control)	---	----	---	----
B-2^0	70	2	---	----
B-3	20	15	---	----
B-4^1	70	2	10000	30
B-5^2	20	15	10000	30
B-6^3	70	2	10000	30

Table 4.1. Continued

Treatment	EtOH [v/v]	[α]Soaking Time [min]	$CaCl_2$ [ppm]	[β]Soaking Time [min]
B-7[4]	20	15	10000	30
B-8[5]	70	2	10000	----
B-9[6]	20	15	10000	----

[α]In ethanol; [β]In Ca^{+2}; [0]EtOH 70%/2 min: (soaked in ethanolic solution (70% v/v) for 2 minutes); [1]Ca^{+2}/30min then EtOH 70%/2min (soaked in $CaCl_2$ (10000 ppm) for 30 minutes and then transferred to an ethanolic solution (70% v/v) and soaked for 2 minutes); [2]Ca^{+2}/30min then EtOH 20%/15min;) [3]EtOH 70%/2min then Ca^{+2}/30min; [4]Ca^{+2}/30min then EtOH 20%/15min; [5] EtOH 70% + Ca^{+2} for 2 min; [6] EtOH 20% + Ca^{+2} for 15 min.

Some considerations for the chosen the pre-treatments were:

- The sample to solution ratio was 6 slices per 100 mL of solution.
- Raw potatoes without pre-treatment (soaking) were used as the control.
- Immediately after the pre-treatment, the samples were blotted with paper towel prior to frying.
- Samples soaked for 2 and 15 minutes in 70% (v/v) and 20% (v/v) ethanolic solutions respectively, dehydrated to nearly the same levels, losing around 8% of water (w/w) for either treatment.
- Pre-treatments B-2 and B-3 evaluate the effect of sample dehydration only.
- Pre-treatments B-4 and B-5 evaluate the effect of tissue firming by Ca^{+2} before dehydration takes place.
- Pre-treatments B-6 and B-7 evaluate the effect of ethanolic dehydration before tissue firming by Ca^{+2} takes place.

- Pre-treatments B-8 and B-9 evaluate the combined effect of ethanolic dehydration and tissue firming by Ca^{+2} taking place simultaneously.

After frying, all samples were stored in Mason jars for subsequent product quality attribute tests.

4.4.3 Thermal treatment for enzymatic activation

The effect of heat for activation of the pectin methyl-esterase (PME) enzymes to increase the number of free carboxylic groups in the pectic substances to allow exogenous Ca^{+2} crosslinking was evaluated. To activate the native PME, potato slices (1 layer) of 1 ± 0.05 mm in thickness and 50.4 mm diameter were sealed in an air tight plastic bag (80µm thick) and submerged in a water bath pre-heated at 50.0ºC and let to stand at this temperature for 30 minutes. Following the thermal treatment, the samples were removed from the bags and sprayed on both sides with a calcium chloride solution (10000 ppm) and allowed to rest for 60 minutes. Then the samples were blotted with paper towel following immediate frying. After frying, all samples were stored in Mason jars for subsequent product quality attribute tests.

4.4.4 Sonication

The effect of the use of ultrasound to enhance Ca^{+2} impregnation into the potato tissue without thermal pre-treatment (D-1) and with thermal pre-treatment (D-2) was evaluated as follows.

4.4.4.1 Sonication without thermal pre-treatment

Potato slices (1 ± 0.05 mm thick and 50.4 ± 1 mm diameter), were inserted in an airtight plastic bag containing calcium chloride ($CaCl_2$) solutions at concentrations of

1000, 5000, 10000, and 20000 ppm at simultaneous soaking and sonication times of 10 and 30 minutes. The sample to solution ratio was 16 slices per 100 mL of solution. Raw potatoes without undergone soaking and sonication pre-treatments were used as the control. At soaking periods of 10 and 30 min. Immediately after the sonication pre-treatment, the samples were blotted with paper towel following immediate frying. After frying, all samples were stored in Mason jars for subsequent product quality attribute tests.

4.4.4.2 Sonication with thermal pre-treatment

The effects of sonication combined with PME activation and Ca^{+2} (Heat So Ca^{+2}) were evaluated. As for controls, these other pre-treatments were carried out as well:

a) Sonication combined with Ca^{+2} (So Ca^{+2});
b) PME activation and Ca^{+2} (Heat Ca^{+2});
c) Raw samples not pre-treated;

For PME activation, potato slices (1 layer) of 1 ± 0.05 mm in thickness and 50.4 ± 1 mm diameter were sealed in an air tight plastic bag (80μm thick) and submerged in a water bath pre-heated at 50.0ºC and let to stand at this temperature for 30 minutes.

For the sonicated samples, immediately after they were sprayed on both sides with a $CaCl_2$ solution (10000 ppm), they were inserted inside airtight plastic bags and sonicated for 60 minutes. Then the samples were blotted with paper towel following immediate frying. After frying, all samples were stored in Mason jars for subsequent product quality attribute tests.

4.5. Pre-treatments

Based on the preliminary study for pre-treatments on Section *4.3.4*, the following pre-treatments were chosen to be carried out for optimization studies:

A mono-layer containing 16 potato slices (1.0 ± 0.05 mm) was organized inside a Bisphenol-A (BPA) free bag (Food Saver Co.), 80μm thick (Mitutoyo Thickness Gage, Japan), and 100 mL of fluid medium (RO water or calcium chloride solution) was added to the samples. This ratio (16 slices/100 ml) would insure no dilution of the liquid medium during the treatment time.

Five concentrations of calcium chloride were used to pre-treat the samples, 0 ppm (RO water), 1000 ppm, 5000 ppm, 10000 ppm, 20000 ppm, and 50000 ppm. For each of these concentrations, three treatment times were used: 5, 10, and 30 minutes. And for each concentration and time, two treatments were used, sonication on the water bath, and no-sonication on the same water bath, keeping the same temperature. Once the treatment time was over, the samples were removed from the bags, blotted dry using a paper towel, and then fried. Each assay was carried out in triplicate (Table 4.2).

Table 4. 2. Experimental design.

Treatment	**Treatment time [minutes]**	**Calcium Chloride concentration [10^3ppm]**
Non-Sonicated	0 (control)	No treatment
Sonicated	5, 10, 30	0 (control), 1, 5, 10, 20, 50
Non-Sonicated	5, 10, 30	0 (control), 1, 5, 10, 20, 50

4.6. Frying experiments

A commercial deep-fat fryer (George Foreman Spin Fryer –GSF026B) was used in this study. The fryer has a capacity of 2.6 L of oil and has a centrifuge system coupled to a sample basket. A tachometer (Laser Photo/Contact Tachometer with IR Thermometer - Model RPM Extech Instruments) was used to determine the linear rotational speed of the centrifuge. The speed of 457±1 rpm was used throughout the experiments. The relative centrifugal force (RCF), commonly referred to as "g-force" or "times g", was calculated to be 13.8 times g at the center of the sample which sits at a distance of 0.06 m from the center of the centrifuge. Fresh canola oil was used for all the experiments.

Four slices of potato chips were loaded into the fryer basket. A circular (25 cm diameter) aluminum mesh screen was placed in the basket, above the samples, to make sure the samples will be kept submerged while being fried in the hot oil (Figure 4.3). Once the oil reached the target temperature (165.0 ºC) at atmospheric pressure (101 kPa), the basket was lowered and consequently the samples were submerged into the oil. The samples were fried for 1 minute and 25 seconds, to assure their doneness, where their moisture content (w.b.) reached 2% or below. At the end of the frying time, the basket was lifted up from the oil and the centrifugation process was activated immediately for the next 40 seconds (optimum time to remove surface oil according to preliminary results). After the centrifuging step, the chips were unloaded from the basked, allowed to cool down for 2 minutes at room temperature and then they were stored in mason glass jars, at room temperature, properly labeled, for further analysis.

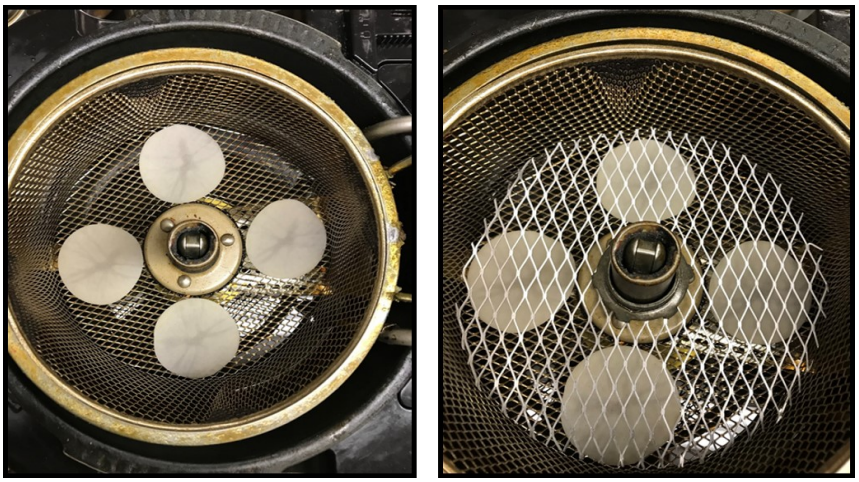


Figure 4. 3. Sample loading into the fryer basket prior to frying.

For the preliminary pre-treatment tests, potato samples were fried at atmospheric pressure at 175.0°C for 55 seconds or until the final product moisture reached 2% w.b. or below. The temperature used in the preliminary pre-treatment frying tests was based on the recommendations from the "*Guidance for Industry Acrylamide in Foods*" from the U.S. Department of Health and Human Services and FDA. This guidance suggests a range of possible approaches to acrylamide reduction. Thermal input, higher temperatures and longer cooking times can increase acrylamide formation in potato chips. In particular, acrylamide formation increases at the end of the frying process, as moisture content falls, e.g., below 3 percent (Medeiros Vinci et al., 2012).

Based on frying time and temperature used during the preliminary tests, an increase of 10.0ºC in the frying temperature reduced the frying time by 30 seconds, thus from 85 seconds at 165.0ºC to 55 seconds at 175.0ºC. It is known that lower frying temperatures in process like vacuum frying produces less acrylamide (Granda et al.,

2004). Although the acrylamide content was not measured, the slightly lighter potato chips colors produced at 175.0ºC was considered to potentially have a lower acrylamide content. The effects of a slightly higher temperature in the production of acrylamide could have been offset by the considerably lower processing time for the 1 mm thick potato slices. Some U.S. potato chip manufacturers have adopted recommendations (Morales et al., 2008) to set fryer temperatures to 175ºC or below, depending on the product and the frying system (SFA, 2010) to reduce acrylamide content. Frying at lower temperatures (e.g., below 170ºC) may cause higher fat uptake and affect crispness (Morales et al., 2008; SFA, 2010). In summary, the ultimate goal of this study was to develop a process to reduce the oil content of chips because of the increase demand of consumer for healthier snacks. Acrylamide content could be another issue addressed here since there is a great health concern on this topic for these types of food-products.

4.7. Optimization of pre-treatments to reduce potato chip oil content using response surface methodology

Pre-treatment optimum operation conditions was investigated to minimize oil uptake in potato chips. The effect of ultrasound waves, time, and calcium chloride concentration on the final oil content of deep-fat fried potato chips was evaluated. Response surface methodology (RSM) was used to evaluate the results of the central composite design (CCD) for the oil content response as a function of time (3 levels), calcium chloride concentration (5 levels) and the use of sonication or lack of thereof (2 levels). The JMP® Pro v. 13.1.0 statistic software was used for this evaluation.

4.7.1 Optimization design and desirability function

Pre-treatment optimum operation conditions was investigated with the goal of minimizing oil uptake in potato chips. The effect of ultrasound waves, time, and calcium chloride concentration on the final oil content of deep-fat fried potato chips was evaluated. Response surface methodology (RSM) was used to evaluate the results of the central composite design (CCD) for the oil content response as a function of time (3 levels), calcium chloride concentration (5 levels) and the use of sonication or lack of thereof (2 levels). A statistical model representing the influence of those factors (time, concentration, sonication or lack of thereof) on the response dependent variable (oil content of the potato chips) was developed and validated using analysis of variance (ANOVA).

The desirability function (Derringer and Suich, 1980) was applied to optimize simultaneously the response variables. This function was used to transform the estimated response variable, calculated by the fitted response surface associated with CCD experimental design, into a desirable value (di), according to Eq. 4.1.

$$d_i = \begin{cases} 0 & \hat{y}_i \le y_{i\,min} \\ \left[\dfrac{\hat{y}_i - y_{i\,min}}{y_{i\,max} - y_{i\,min}} \right] & y_{i\,min} < \hat{y}_i < y_{i\,max} \\ 1 & \hat{y}_i \ge y_{i\,max} \end{cases} \qquad 4.1$$

where $y_{i\ min}$ and $y_{i\ max}$ are the minimum and maximum acceptable value of $\hat{y}_i$, respectively. The values of d_i vary in the interval $0 \le d_i \le 1$, increasing as the desirability of the

corresponding response increases. The individual desirabilities were then combined using the geometric mean to give an overall desirability (*D*) (Eq. 4.2).

$$D = (d_1 \times d_2 \times \ldots \times d_k)^{1/k} \quad 4.2$$

The overall desirability was analyzed using a univariate search technique to optimize *D* over the independent variable domain, which resulted in the desirability of the combined responses levels.

4.7.2 Experimental design

A Central composite of RSM for a three-variable experimental design was carried out. The independent factors considered were bath time (X_1: 5, 10, 30 minutes), calcium chloride concentration (X_2: 1.0, 5.0, 10.0, 20.0, and 50.0 x 10^3 ppm), and sonication or lack of thereof (X_3: S/NS). The dependent variable was the oil content of the potato chips in dry basis. This resulted on a factorial 3x5x2 design, therefore 30 data for the response variable were inputted, and each came from an average observation of 3 replicates measured analytically.

The results of the pre-treatment independent variables for the response variable oil content, according to the corresponding combination of the independent variables and their levels were used to run the CCD analysis (Table 4.3).

Table 4. 3. Factorial design (3x5x2) for the response variables.

X_1 [min]	X_2 [10^3 ppm]	X_3	Oil content [% d.b.]
5	1	S	y_1
10	1	S	y_2
30	1	S	y_3
5	5	S	y_4
10	5	S	y_5
30	5	S	y_6
5	10	S	y_7
10	10	S	y_8
30	10	S	y_9
5	20	S	y_{10}
10	20	S	y_{11}
30	20	S	y_{12}
5	50	S	y_{13}
10	50	S	y_{14}
30	50	S	y_{15}
5	1	NS	y_{16}
10	1	NS	y_{17}
30	1	NS	y_{18}
5	5	NS	y_{19}
10	5	NS	y_{20}
30	5	NS	y_{21}
5	10	NS	y_{22}
10	10	NS	y_{23}
30	10	NS	y_{24}
5	20	NS	y_{25}
10	20	NS	y_{26}
30	20	NS	y_{27}
5	50	NS	y_{28}
10	50	NS	y_{29}
30	50	NS	y_{30}

Three different case-models were used to obtain the desirability functions: The first (1) included all main factors (X_1, X_2, X_3). The second (2) and the third (3) models did not include the X_3 term, two analyses were carried out separating the responses for

the non-sonicated samples (NS), and sonicated (S) one, respectively. The models constructed for the RSM for all three cases included the main factors (X_1, X_2, X_3), their quadratic terms (X_1*X_1, X_2*X_2, X_3*X_3), and their cross-product (X_1*X_2, X_1*X_3, X_2*X_3).

4.8. Analytical methods

4.8.1 Oil content

The oil content of the potato chips was determined using the Soxtec System HT extraction unit (Pertorp, Inc., Silver Spring, MD) with petroleum ether as solvent (AACC, 1986). About three grams (3 g) of ground potato were weighed (W_p), placed on a cellulose extraction thimble (model 2800256, Whatman, England), and covered with a de-fatted cotton ball. Six extractions were performed at each time. Aluminum cups were dried for 15 minutes at 105ºC and cooled in a desiccator for 20 minutes. The cup weight (W_1) was recorded, and 50 mL of petroleum ether was added to each cup. The samples were then subjected to extraction (40 minutes at 95ºC and the same time was used to rinse the samples), and the oil from the chips collected into those aluminum cups. Petroleum ether was recovered using a condensation system built into the equipment for circulation. To make sure all the petroleum ether was evaporated, the cups were dried in a convection oven for 20 minutes at 105ºC. The cups were then cooled in a desiccator for 20 minutes, and the final cup weight was recorded (W_2). All the tests were conducted in triplicate. Finally, the oil content (OC, wet basis) was obtained using Eq. 4.3:

$$OC(\%) = 100 \times \frac{W_2 - W_1}{W_p} \quad 4.3$$

where W_2 is the weight of the cup after oil extraction and W_1 weight of the cup before oil extraction, and W_p is the weight of the sample.

4.8.2 Moisture content

Moisture content of fried samples (3 grams) was measured using a vacuum oven (Squared Lab Line Instruments, Melrose Park, IL, USA) set at 70ºC for 6 hours or until constant weight of the samples was reached. The method is described in the method 930.04 (AOAC, 1990). Measurements were made in triplicate.

4.8.3 Specific gravity

The specific gravity of the potatoes was measured using a slightly modification of the weight in air/weight in water method (Gould, 1995). Each potato was weighed individually in a custom-made system (Figure 4.4) that consisted of a thin wire basket placed under inside a beaker with pure water on top of an analytical scale (0.01 g resolution, Sartorius, Wood Dale, IL). The weight in air (W_a) was obtained by placing the potato directly over the scale. The weight in water (W_w) was determined by submerging the potato in the pre-tared basket under water. The specific gravity was determined by the Eq. 4.4:

$$\left(SG = \frac{W_a}{W_w}\right)_{T_{constant}} \quad 4.4$$

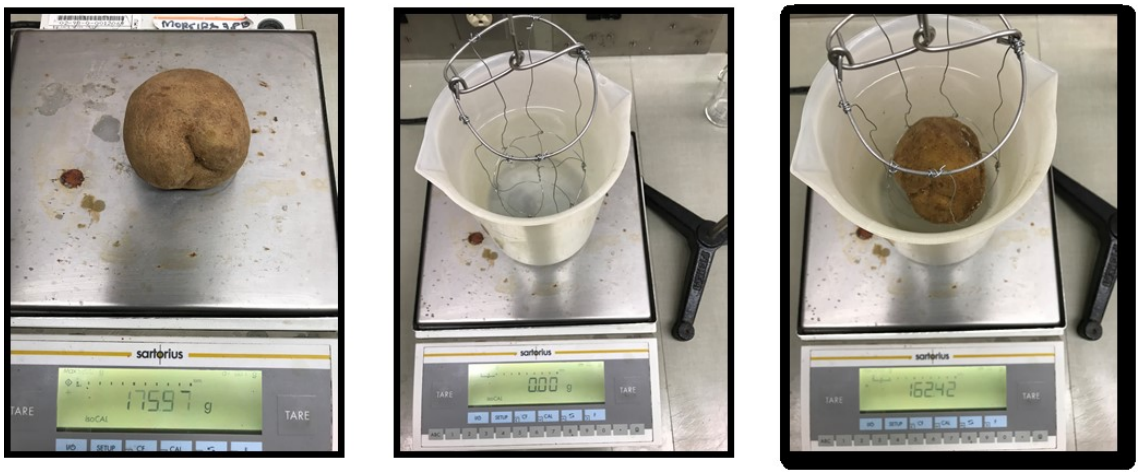


Figure 4. 4. Custom made specific gravity apparatus for individual tubers.

4.9. Product quality attributes

4.9.1 Color

A Labscan XE colorimeter (Hunter Lab, Inc., Reston, VA, USA) with the Universal v.3.73 software was used to evaluate the fried products color using the CIELAB system. The measuring aperture diameter was 1.25 inches, the illuminant was the D65, and 10º for the observer was chosen. The colorimeter was calibrated using standard white and black tiles. Sixteen (16) randomly samples were evaluated and five readings were recorded as an average reading for each sample. Mean values of the coordinates L* (lightness–darkness), a* (redness–greenness), and b* (yellowness–blueness) were used to determine the color of the product through reflectance mode.

4.9.2 Texture

The texture of the potato slices was measured at room temperature using a Brookfield TA-CT3 equipment. A 30 grams ball stainless steel probe (TA-18) of 12.7 mm diameter was used to move through the samples causing its rupture. A base table

with a hollow fixture plate (2-point support - 0.018 m hollow TA-DEC Pot) was used to hold the sample still. Once the probe touched the sample and sensed it (0.07 N of trigger force), it would travel through it (compression mode) at a speed of 0.1 mm/s causing the sample to fracture. The force data in Newtons was logged at a rate of 200 points per second through the TexturePro CT v 1.2 Build 9 software. The maximum force recorded just before the breaking point, was defined as "hardness" (Steffe, 1996) of the samples. Sixteen samples were used per each treatment.

4.9.3 Solids density

To obtain the solid volume of potato chips, the pre-weighed and de-fatted samples were manually ground using a mortar and placed in a compressed helium gas multi-pycnometer (Quantachrome & Trade, NY, USA). Solids density, ρ_s (kg/m^3), was determined by dividing the weight of the sample by its solid volume. The test was performed in triplicate.

4.9.4 Bulk density (apparent density)

The bulk volume was measured using the liquid displacement technique with 10% alcohol solution on a custom-built apparatus (Da Silva and Moreira, 2008). Bulk density, ρ_b (kg/m^3), was then determined by dividing the weight of the chip by its bulk volume. The test was performed in triplicate.

4.9.5 Porosity

Porosity, φ, was calculated as:

$$\varphi = 1 - \frac{\rho_b}{\rho_s} \qquad 4.5$$

4.9.6 Degree of shrinkage (D)

The diameter of the samples after frying was measured using a digital steel caliper (MG Tool Co., New York, NY, USA), with. 0.01 mm of resolution. The degree of diameter shrinkage (D) was calculated by:

$$D = \frac{d_o - d_f}{d_o} \quad 4.6$$

Where d_o is the original diameter of raw sample and d_f is the diameter of the sample after frying, both in the same dimension units. Sixteen samples were used for each experiment.

4.10. Sensory evaluation

A 32-member consumer panel (randomly selected faculty, students, and staff) at Texas A&M University was used to make the sensory evaluation of the potato chips. The quality attributes evaluated were appearance, color, odor, texture, flavor, and overall quality. See example in Figure 4.5. Panelists scored the samples using a nine-hedonic scale (Da Silva and Moreira, 2008), where a score of 1 represented attributes most disliked and a score of 9 represented attributes most liked. Scores higher or equal to 5 were considered acceptable.

Three different treatments were evaluated: (1) The control (fried chip, no treatment); (2) chips sonicated in calcium chloride (food grade - Paris Gourmet, Cuisine Tech) solution at 20 x 10^3 ppm for 30 minutes; (3) and chips non-sonicated in calcium

chloride (food grade - Paris Gourmet, Cuisine Tech) solution at 20 x10^3 ppm for 30 minutes.

The samples were randomly distributed to the panelists, one at a time, with randomly selected 3 digits codes. They were salted (2 g of sea salt per 100g of fried chips), and a cup of water was given to the panelists to rinse their mouth and clean their palate between sample trials. The panelists were asked to evaluate the samples individually, meaning that no comparison among the samples were permitted.

4.11. Mass transfer during the pre-treatment

Prior to pre-treatment, 8 slices of raw potatoes were numbered with a permanent marker, weighted in an analytical balance (Sartorius, 0.0001 g resolution, Wooed Dale, IL) and weighted after the pre-treatment (soaked in calcium chloride solution at the various concentrations, sonicated and not sonicated).

4.12. Images using optical microscope

Sample images were taken using an Inverted Optical Microscope (Nikon Eclipse TS-100) using objectives of 10x and 20x magnification. Digital images were acquired by the software and post-processed using the Nikon software (CFI160 Infinity Optical System, Nikon, Japan).

Sensory Evaluation of Potato Chips

Instructions: Please evaluate each sample for each quality parameter and use the number scale below to mark the box which you feel best describes how you like/dislike the sample. Please take a sip of water in between sample evaluations to clean your palate. **DO NOT compare the samples, evaluate them individually**. If you have any additional comment, please write them below.
Thank you for your honest evaluation!

Dislike extremely	Dislike very much	Dislike moderately	Dislike slightly	Neither Like nor Dislike	Like slightly	Like moderately	Like very much	Like extremely
1	2	3	4	5	6	7	8	9

Sample # 468	Appearance	Color	Odor	Texture	Flavor	Overall Quality

Comments:_____

Sample # 796	Appearance	Color	Odor	Texture	Flavor	Overall Quality

Comments:_____

Sample # 354	Appearance	Color	Odor	Texture	Flavor	Overall Quality

Comments:_____

Figure 4. 5. An example of the sensory evaluation sheet used in this study.

4.13. Temperature mapping in the sonicator bath

Measurements of temperature distribution and build up during operation of the ultrasound bath were acquired thought a data logger equipment (OMB Daq54) from OMEGA Engineering Inc. A 3-point temperature calibration of the thermocouples (K-type) was carried out to assure accuracy among the thermocouple readings. Two bulb thermometers were used as reference for the calibration. All the thermocouple readings

were recorded simultaneously to a disk file through the datalogger interface software (OMB-DAQ 54/55/56).

4.14. Statistical data analysis

Statistical data analysis was performed using the JMP® Pro v. 13.1.0 statistic software. Figure plots were made using the 2016 MS Excel® software and the MathWorks MATLAB R2018a (9.4.0.813654) software.

4.14.1 Fit statistics for model comparison - definition

The fit-statistic parameters used for comparing multiple models using the statistic software JMP® Pro v. 13.1.0, are: AICc, AICc Weight, BIC, SSE, MSE, RMSE, and R-Square, and are defined below.

(1) AICc: the Akaike information criterion (AOC) gives a measure of the goodness of fit of an estimated statistical model that can be used to compare two or more models. AICc is a modification of the AIC adjusted for small samples. AICc can only be computed when the number of data points is at least two greater than the number of parameters. The model with the lowest AICc value is the best:

$$AIC_C = AIC + \frac{2k^2+2k}{n-k-1} \quad 4.7$$

(2) AICc Weight: gives normalized AICc values that sum to one. The AICc weight can be interpreted as the probability that a particular model is the true model given that one of the fitted models is the truth. Therefore, the model with the AICc weight closest to one is the better fit. The AICc weights are calculated using only non-missing AICc values, as in Eq 4.8:

$$AIC_c Weight = \frac{e^{\lfloor -0.5\left(AIC_c - min(AIC_c)\right)\rfloor}}{sum\left(e^{\lfloor -0.5\left(AIC_c - min(AIC_c)\right)\rfloor}\right)} \quad 4.8$$

Where min(AICc) is the smallest AICc value among the fitted models. The AICc Weight column is then sorted in decreasing order.

(3) BIC: the Bayesian information criterion (BIC) gives a measure based on the likelihood function of model fit that is helpful when comparing different models. The model with the lower BIC value is the better fit. The BIC is formally defined as (Akaike, 1974):

$$BIC = \ln(n)\, k - 2\ln\left(\hat{L}\right) \quad 4.9$$

where $\hat{L}$ = the maximized value of the likelihood function of the model M, i.e. $\hat{L} = p(x|\hat{\theta},\mathrm{M})$, where $\hat{\theta}$ are the parameter values that maximize the likelihood function; x = the observed data; n = the number of data points in x, the number of observations, or equivalently, the sample size; k = the number of parameters estimated by the model. For example, in multiple linear regression, the estimated parameters are the intercept, the q slope parameters, and the constant variance of the errors; thus, $k = q + 2$.

(4) SSE: the sum of the squared differences between each observation and its predicted value or the residual sum of squares (RSS):

$$SSE = \sum_{i=1}^{n}\left(Y_i - \hat{Y}_i\right)^2 \quad 4.10$$

where Y_i is the observed data value and $\hat{Y}_i$ is the predicted value from the fit.

(5) MSE: gives the average of the squares of the errors of each value:

$$MSE = \frac{1}{n}\sum_{i=1}^{n}\left(Y_i - \hat{Y}_i\right)^2 \quad 4.11$$

(6) RMSE: the square root of the MSE that estimates the standard deviation of the random error.

$$RMSE = \frac{\sqrt{\sum_{i=1}^{n}(Y_i - \hat{Y}_i)^2}}{n} \quad 4.12$$

(7) R-square (R^2): the coefficient of determination, R^2, estimates the proportion of variation in the response that can be attributed to the model rather than to random error. The model with the R-Square value closest to one is the better fit.

$$R^2 = 1 - \frac{SSE}{SST} \quad 4.13$$

where SST is the sum of squared errors of our baseline model:

$$SST = \sum_{i=1}^{n}(Y_i - \bar{Y}_i)^2 \quad 4.14$$

CHAPTER V

RESULTS

5.1. Preliminary pre-treatment methods for potato tissue stabilization

The following pre-treatments to reduce oil uptake in potato chips were evaluated:

5.1.1 Soaking (A)

The final oil content of potato chips that were soaked calcium chloride ($CaCl_2$) solutions for 10 and 30 minutes is shown on Figure 5.1 and Table 5.1. Raw potatoes without the pre-treatment were used as the control.

For soaking times of 10 minutes, the oil content of the samples did not change significantly ($p > 0.05$) (see Table 4.1 for statistical results) from the control samples, only for the samples with concentrations of 20000 ppm of $CaCl_2$, which showed a 18.4% decrease in oil content. All pre-treated samples differed significantly ($p < 0.05$) in oil content values for each $CaCl_2$ concentration tested between the 10 and 30 minutes soaking periods. For 30 minutes of soaking time, all the samples yielded significant lower ($p <0.05$) oil content when compared with the control sample. The lowest oil content value was found for the samples treated with the highest concentration of $CaCl_2$ (20000 ppm) for the longest period (30 minutes) which showed a 26.5% decrease in oil content.

This reduction in oil absorption can be attributed to the use of hydrocolloids as gel-forming compounds and calcium chloride as cross-linking agent, which would form a fine net structure that would prevent the oil migration in the potato tissue during the

frying process (Rimac-Brnčić et al., 2004). Similar mechanism could be taking place to the pectic substances on the lamella-media of the cell wall of the cellular material when Ca^{+2} is added. The cross-linking of these substances by the calcium ions could form a tighter barrier, making pores more uniform like vacuum frying, increase interfacial tension at the surface, and also decrease surface roughness, all of which would hinder oil absorption. More explanation on these mechanisms can be found in the literature review section.

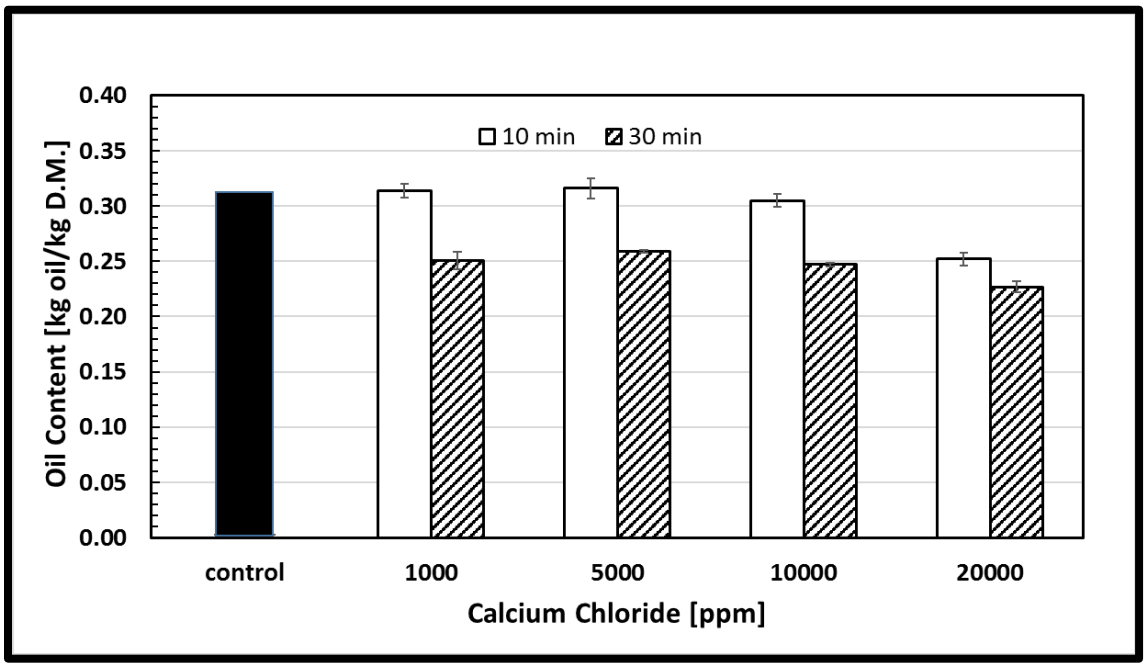


Figure 5. 1. Oil content of potato chips fried at 175ºC/55 seconds and pre-treated with $CaCl_2$ for 10 and 30 minutes soaking times.

Table 5. 1. Statistical results for the oil content of potato chips pre-treated with $CaCl_2$ at 10- and 30-minutes soaking times.

$CaCl_2$ [ppm]	Oil content [kg oil/kg D.M.]	
	10 min	**30 min**
control	$_{x}0.309 \pm 0.003^{a}$	$_{x}0.309 \pm 0.003^{a}$
1000	$_{x}0.314 \pm 0.006^{a}$	$_{y}0.251 \pm 0.008^{b}$
5000	$_{x}0.316 \pm 0.009^{a}$	$_{y}0.259 \pm 0.001^{b}$
10000	$_{x}0.305 \pm 0.006^{a}$	$_{y}0.247 \pm 0.002^{b,c}$
20000	$_{x}0.252 \pm 0.006^{b}$	$_{y}0.227 \pm 0.005^{c}$

Mean values ± standard deviations followed by different letters within the same column^{a-c} are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test. Mean values ± standard deviations followed by different letters within the same row^{x-z} are significantly different ($p < 0.05$) according to the difference Student's t test ($\alpha = 0.05$). Chips were deep-fat fried at 175ºC for 55 seconds at atmospheric pressure.

5.1.2 Dehydration (B)

The oil content of the potato chips that were pre-treated as described in Table 5.2 is shown in Table 5.3 and Figure 5.2. Bars followed by different letters^{a-c} are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test.

All pre-treated samples resulted in less oil absorption (6.5 – 19.0% reduction) when compared with the control samples. No significant differences ($p > 0.05$) were found between the dehydration only treatments (B-2 and B-3). No significant differences ($p > 0.05$) were found whether dehydration took place before or after the Ca^{+2} treatment (B-4 versus B-6 and B-5 versus B-7), however amongst these treatments, the ones with the shorter pre-treatment times periods (32 minutes for B-4 and B-6) absorbed significantly ($p < 0.05$) less oil than the control by 14.4% for B-4, and by 12% for B-6.

Soaking in EtOH 70% (v/v) for only 2 minutes, instead of 15 minutes of EtOH 20% (v/v), besides the 30 minutes for the $CaCl_2$ treatment, was the main difference amongst them.

Pre-treatments B-8 and B-9 were significantly different ($p < 0.05$), with B-8 pre-treated samples absorbing the least amount of oil when compared with all the other pre-treatments. It showed a reduction of 19.0 % when compared with the control. Pre-treatment B-8 had the shortest pre-treatment time, 2 minutes with dehydration and calcium impregnation taking place simultaneously.

Table 5. 2. Pre-treatments for ethanolic dehydration and Ca^{+2} impregnation.

Treatment	**EtOH [v/v]**	**$^{\alpha}$Soaking Time [min]**	**$CaCl_2$ [ppm]**	**$^{\beta}$Soaking Time [min]**
B-1 (control)	---	----	---	----
B-2^0	70	2	---	----
B-3^1	20	15	---	----
B-4^2	70	2	10000	30
B-5^3	20	15	10000	30
B-6^4	70	2	10000	30
B-7^5	20	15	10000	30
B-8^6	70	2	10000	----
B-9^7	20	15	10000	----

$^{\alpha}$In ethanol; $^{\beta}$In Ca^{+2}; ^{0}EtOH 70%/2 min:, ^{1}EtOH 20%/15 min:, $^2Ca^{+2}$/30min then EtOH 70%/2min: (soaked in $CaCl_2$ (10000 ppm) for 30 minutes and then transferred to an ethanolic solution (70% v/v) and soaked for 2 minutes); $^3Ca^{+2}$/30min then EtOH 20%/15min (soaked in $CaCl_2$ (10000 ppm) for 30 minutes and then transferred to an ethanolic solution (20% v/v) and soaked for 15 minutes); ^{4}EtOH 70%/2min then Ca^{+2}/30min; ^{5}EtOH 20%/15min then Ca^{+2}/30min; ^{6} EtOH 70% + Ca^{+2} for 2 min; ^{7} EtOH 20% + Ca^{+2} for 15 min.

From this set of experiments, ethanolic dehydration by itself (B-2 and B-3) resulted in samples with reduced oil content, as observed by Moreno and Bouchon (2008). The combination of Ca^{+2} ions with ethanolic dehydration further hinder oil absorption. Whether dehydration is carried out before (B-6 and B-7) or after (B-4 and B-5) the Ca^{+2} treatment, the oil absorption was not statistically different ($p > 0.05$). However, the samples that had the shorter times for pre-treatment (B-4 and B-6), showed a statistically lower oil absorption ($p > 0.05$). Among all treatments, the 2 minutes pre-treatment using 70% (v/v) EtOH solution combined with Ca^{+2} resulted in the lowest oil absorption.

Table 5. 3. Statistical results for the oil content of potato chips pre-treated by ethanolic dehydration and $CaCl_2$ impregnation.

Treatments	Oil content [kg oil/kg D.M.]
Control (B)	0.337 ± 0.010^{a}
B-2	0.302 ± 0.013^{b}
B-3	0.315 ± 0.011^{b}
B-4	$0.289 \pm 0.006^{b,c}$
B-5	0.300 ± 0.003^{b}
B-6	$0.297 \pm 0.008^{b,c}$
B-7	0.305 ± 0.009^{b}
B-8	0.273 ± 0.014^{c}
B-9	$0.289 \pm 0.008^{b,c}$

Mean values ± standard deviations followed by different letters within the same column[a-c] are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test.

In conclusion, higher alcohol concentration can lead to faster dehydration and lower oil absorption, however the level of dehydration and its effects on oil absorption need to be addressed. Issues may arise if evaporation of the alcohol follows dehydration. The tissue might behave like the freeze-dried samples studied by Gamble and Rice (1987) and Moreno and Bouchon (2008), which showed higher oil absorption when compared to the control. The external porous structure may impose low resistance thus resulting in high oil absorption.

Despite the fact that dehydration decreased oil absorption by itself, Ca^{+2} played a role on this mechanism since it reduced the oil content even further. Dehydration affected the oil absorption (B-8 versus B-9), thus certainly the rate of Ca^{+2} impregnation will be a factor for the final tissue-structure formation. The same reasons given on section "A-soaking" can be attributed as the main mechanisms for the oil absorption phenomena.

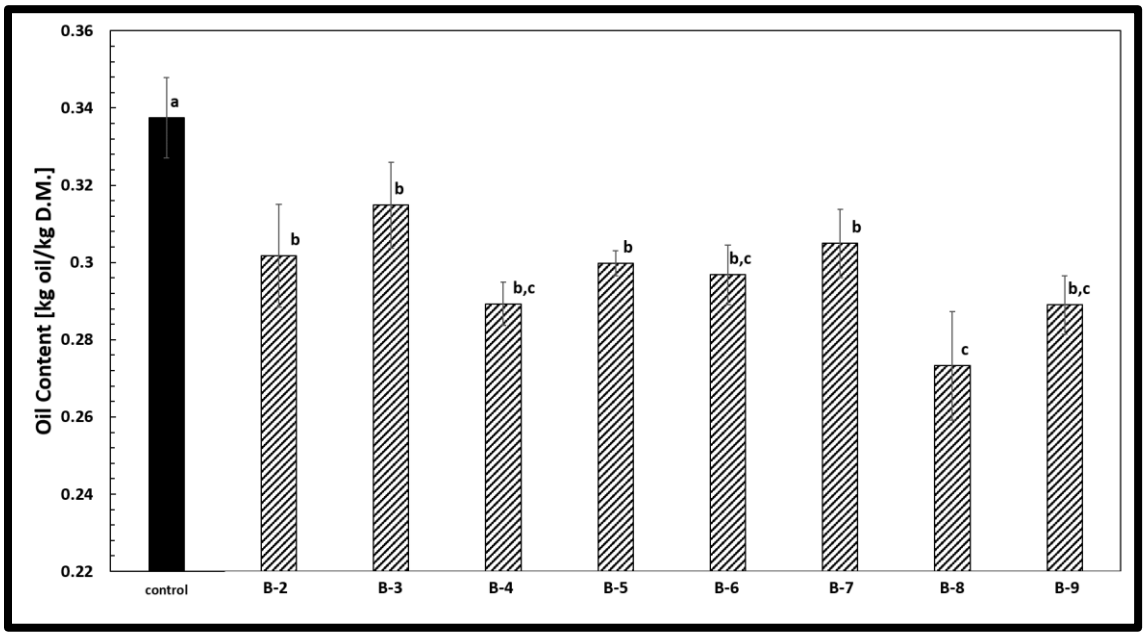


Figure 5. 2. Oil content of potato chips pre-treated with ethanol and $CaCl_2$ at various concentrations and soaking times.

5.1.3 Thermal treatment for enzymatic activation (C)

Table 5.4 and Figure 5.3 show the final oil content of the chips. Bars followed by different letters[a-b] are significantly different according to the difference Student's t test ($\alpha = 0.05$).

Table 5. 4. Oil content of potato chips pre-treated by thermal treatment and Ca^{+2} impregnation.

Treatments	Oil content [kg oil/kg D.M.]
Control	0.30 ± 0.010 [a]
Heat Ca^{+2}	0.27 ± 0.005 [b]

Mean values ± standard deviations followed by different letters[a-b] are significantly different according to the difference Student's t test ($\alpha = 0.05$).

Pre-treated samples showed significant oil content when compared with the control ($p < 0.05$). The oil absorption reduction was about 8.8 %, (see Table 5.4).

Pectins are highly complex polysaccharides abundant in plant primary cell walls. Homogalacturonan pectins, which are major components of the primary cell wall, have a potential for modifications such as methyl-esterification, as well as an ability to form cross-linked structures with divalent cations (Levesque-Tremblay et al., 2015). These mechanisms contribute to changing the mechanical properties of the cell wall, which affects the mechanics of oil absorption since it is a structure-dependent phenomenon.

In this study, the degree of de-methylesterification by the PME activation in the thermal treatment was not evaluated. Neither the level of cross-linking of Ca^{+2} with the pectic substances which would impact the cell wall mechanical properties, was assessed.

PMEs act on HG by either de-methylesterifying residues in the Galacturonic acid chain individually randomly, or linearly blockwise (Markovič and Kohn, 1984). These two modes of action may have inverse consequences on the plant cell wall. When the PMEs act individually randomly, the de-esterification of HGs frees protons promoting the activity of polygalacturonases (Moustacas et al., 1991), but does not allow for the formation of Ca^{+2} bridges. The action of polygalacturonase can, in turn, break down the pectin and contribute to cell wall loosening. When the PMEs act linearly blockwise on HGs, long stretches of negatively charged carboxylate appear, which can interact with Ca^{+2} creating a denser gel structure that would be expected to lead to decreased porosity. Thus, PME activity can strengthen as well as loosen the cell wall (Levesque-Tremblay et al., 2015).

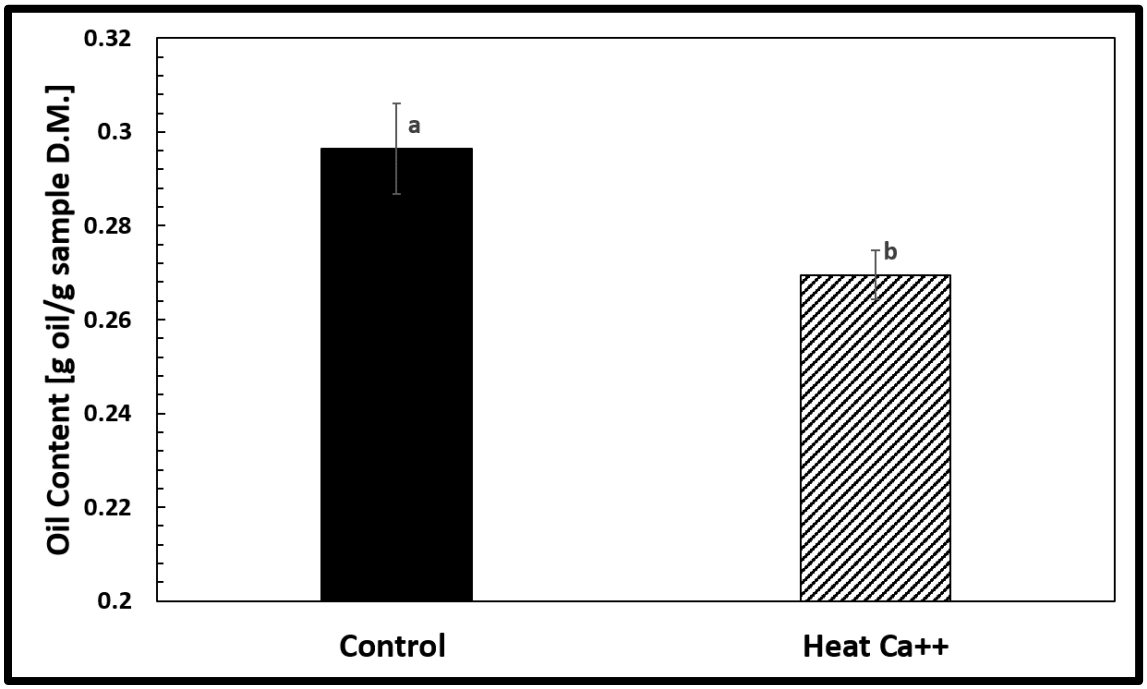


Figure 5. 3. Oil content of potato chips pre-heated and treated with Ca^{+2}.

To evaluate this pre-treatment even further, a couple of approaches could be taken.

- Other combinations of thermal treatments (temperature and time) for the PME activation can be verified, as long as it is on the temperature operating range of the PME (50-70ºC).
- Increase the ionic strength of the soaking solution by increasing the exogenous Ca^{+2} concentration. This approach can be optimized for the degree of decarboxylation of pectin groups achieved during the thermal treatment for the PME activation.

- Enhance the Ca^{+2} ion impregnation in the tissue by using techniques that improve mass transfer in this type of setting.

Other experimental observations have shown that the relationships between the de-methyesterification, the pattern of de-methylesterificaton, its effect on cell wall elasticity, and other biomechanical parameters are not straightforward (Chebli et al., 2012; Levesque-Tremblay et al., 2015). A more fundamental work on this area would be needed to understand these mechanisms in a cellular level rather than analyzing experimental results and oil content output results.

5.1.4 Sonication (D)

5.1.4.1 Sonication without thermal pre-treatment (D-1)

D-1 pre-treatment follows the same settings laid out for pre-treatment "**A**" (**Soaking**) mentioned before in Chapter IV. However, ultrasound was used to enhance Ca^{+2} impregnation into the potato tissue

Table 5.5 and Figure 5.4 show the final oil content of potato chips that were pre-treated before frying at atmospheric pressure (175.0ºC/55 seconds) with calcium chloride solutions at concentrations of 1000, 5000, 10000, and 20000 ppm at simultaneous soaking and sonication times of 10 and 30 minutes. Raw potatoes without undergone soaking and sonication pre-treatment were used as the control.

Table 5. 5. Oil content of potato chips pre-treated with $CaCl_2$ at 10 and 30 minutes of sonication.

$CaCl_2$ [ppm]	Oil content [kg oil/kg D.M.]	
	10 min (Sonicated)	**30 min (Sonicated)**
control	$_{x}0.315 \pm 0.001^{a}$	$_{x}0.315 \pm 0.001^{a}$
1000	$_{x}0.304 \pm 0.008^{a,b}$	$_{y}0.252 \pm 0.003^{b}$
5000	$_{x}0.309 \pm 0.012^{a,b}$	$_{y}0.238 \pm 0.002^{b,c}$
10000	$_{x}0.283 \pm 0.004^{b,c}$	$_{y}0.232 \pm 0.003^{c}$
20000	$_{x}0.272 \pm 0.004^{c}$	$_{y}0.220 \pm 0.001^{c}$

Mean values ± standard deviations followed by different letters within the same column^{a-c} are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test. Mean values ± standard deviations followed by different letters within the same row^{x-z} are significantly different ($p < 0.05$) according to the difference Student's t test ($\alpha = 0.05$).

For sonication periods of 10 and 30 minutes, the oil content of the samples decreased significantly ($p < 0.05$) from the control samples for all the concentrations of $CaCl_2$ tested. All pre-treated samples differed significantly ($p < 0.05$) in oil content values for each $CaCl_2$ concentration tested between the 10 and 30 minutes sonication periods. Samples treated for 30 minutes of sonication showed lower values for oil content (20-24% lower) when compared with samples treated for 10 minutes of sonication. The lowest value for oil content (0.220 ± 0.001 kg oil/kg D.M) was found for the longest sonication period treatment (30 minutes) and the highest $CaCl_2$ solution concentration (20000 ppm). Statistical results are shown on Table 5.5.

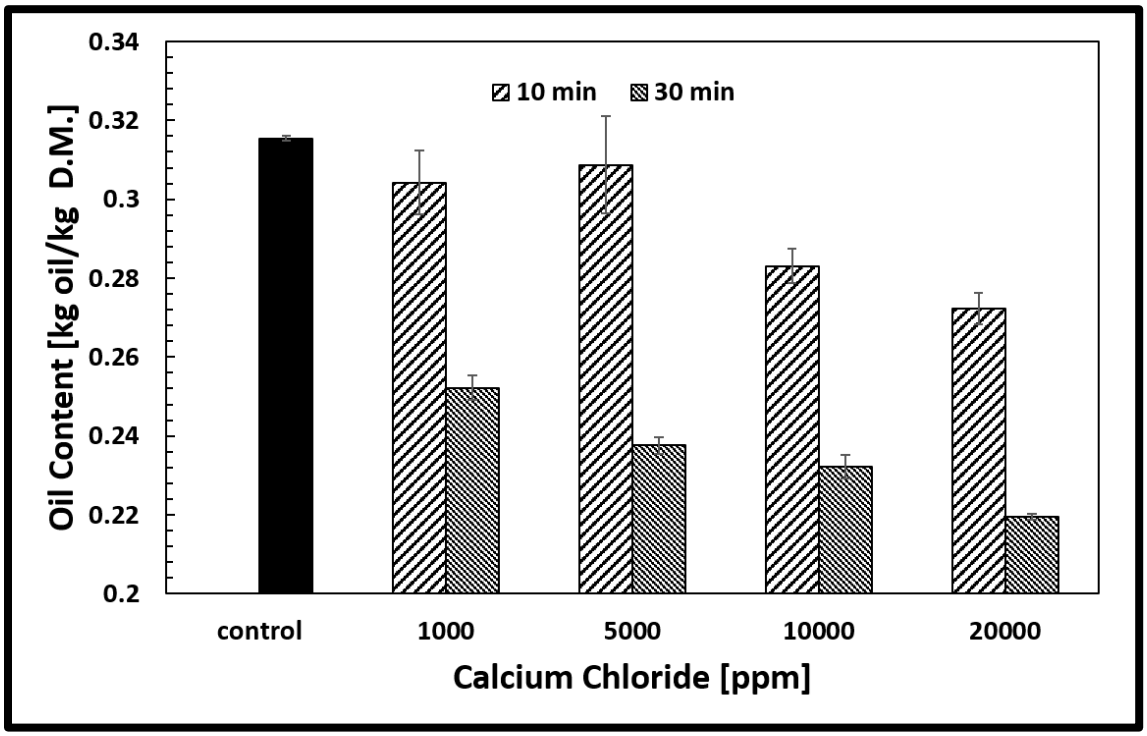


Figure 5. 4. Oil content of potato chips pre-treated with $CaCl_2$ and sonicated for 10 and 30 minutes soaking times.

5.1.4.2 Sonication with thermal pre-treatment (D-2)

D-2 pre-treatment follows the same settings laid out for pre-treatment "**C**" (**Thermal treatment for enzymatic activation)** mentioned above. However, to enhance Ca^{+2} impregnation into the potato tissue, the use of ultrasound waves was employed as part of the treatment.

The effects of sonication combined with PME activation and Ca^{+2} (Heat So Ca^{+2}) were evaluated. As for controls, these other pre-treatments were carried out as well:

- Sonication combined with Ca^{+2} (So Ca^{+2});
- PME activation and Ca^{+2} (Heat Ca^{+2});
- Raw samples not pre-treated;

Table 5.6 and Figure 5.5 show the final oil content of the chips for the 4 pre-treatments. Bars followed by different letters[a-c] are significantly different ($p < 0.05$) according to the difference Student's t test ($\alpha = 0.05$).

Table 5. 6. Statistical results for the oil content of potato chips pre-treated (Ca^{+2}, PME activated, sonicated).

Treatments	Oil content [kg oil/kg D.M.]
Control	0.296 ± 0.010^{a}
So Ca^{+2}	$0.276 \pm 0.018^{a,b}$
Heat Ca^{+2}	$0.270 \pm 0.005^{a,b}$
Heat So Ca^{+2}	0.252 ± 0.014^{b}

Mean values ± standard deviations followed by different letters within the same column[a-c] are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test. So = sonicated; Heat (PME activation 50ºC/30min).

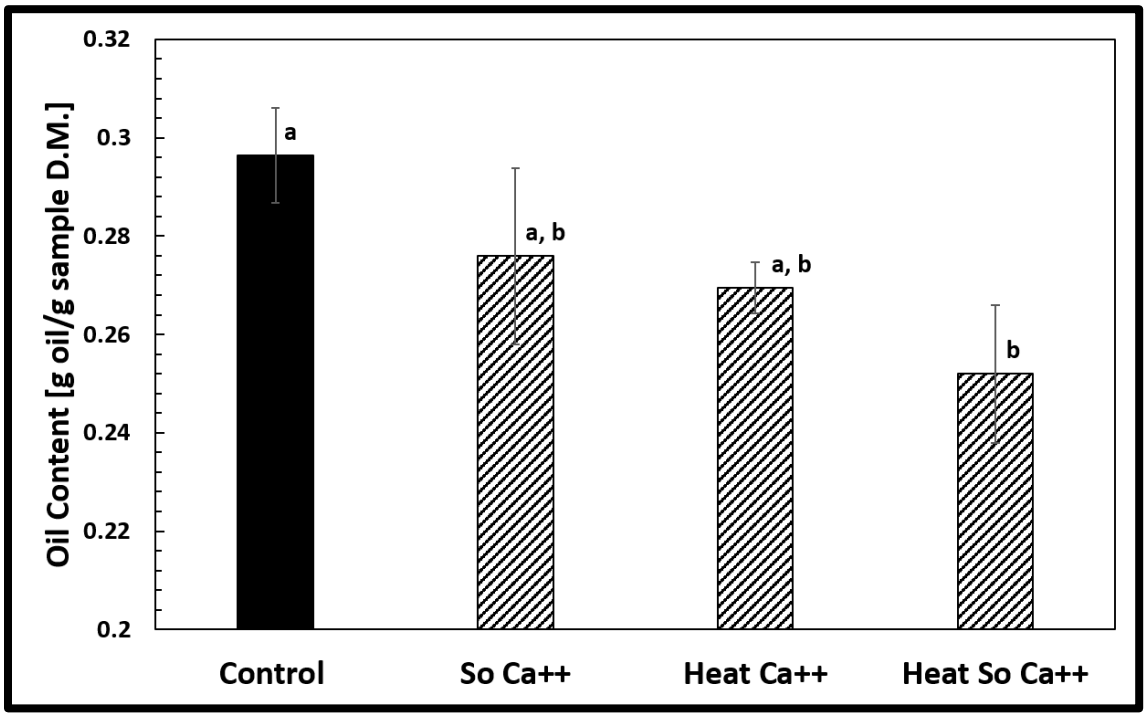


Figure 5. 5. Oil content of potato chips pre-heated, treated with Ca^{+2}, and sonicated

All pre-treated samples absorbed significantly ($p < 0.05$) less oil than the control (6.8 % to 14.9 % reduction). There were no significant ($p > 0.05$) differences between sonicated (So Ca^{+2}) and heat-treated (Heat Ca^{+2}) samples treated with Ca^{+2}, yielding an oil reduction of 6.8 - 8.8 % when compared to the control. However, when all three factors were combined in to the pre-treatment (heat for PME activation, sonication, and Ca^{+2}), the lowest oil absorption was found (0.252 ± 0.014 kg oil/ kg D.M.), resulting in an oil reduction of 14.9% when compared with the control.

5.1.5 -Summary of the preliminary pre-treatment results

5.1.5.1 Soaking (A)

All the samples pre-treated with Ca^{+2} showed a reduction in oil absorption. The higher the Ca^{+2} concentration and the longer the soaking period, the lower the oil absorption. Possibly because the impregnation process of soaking the samples in Ca^{+2} solutions was being effective in binding exogenous Ca^{+2} with pectin substances in the lamella media of the cellular tissue. This would confer more rigidity to the cell walls of the tissue and better adhesion among the cells, diminishing rupture/de-attachment of cells during the violent process of deep-fat frying. Therefore, a lower oil absorption of the fried product would take place. The highest reduction in oil content compared to the control was 26.5%.

5.1.5.2 Dehydration (B)

Dehydration of samples pre-treated with higher concentration ethanolic solutions and the addition of Ca^{+2} ions produced lower oil content chips. This behavior can be attributed for its properties of fixation and dehydration while preserving the integrity of the cellular structure. Although the use of alcohol in the food industry may not face barriers such as religious and ethnical, since it will be mostly evaporated after frying, higher processing costs might be a determining factor for its use. Added cost for alcohol losses due to evaporation during frying or for its recovery, might not be feasible to the industry. Regardless of these issues, this study offers the scientific possibility of its use as an alternative for heated-forced air drying (shrinkage) and osmotic dehydration

(added solutes) for food materials. The highest reduction in oil content compared to the control was 19.0%.

5.1.5.3 Thermal treatment for enzymatic activation (C)

Heat treating samples to activate PME enzymes and promote decarboxylation of pectic substances to facilitate Ca^{+2} ions cross-link made a significant impact on the sample oil uptake. The products absorbed significantly less oil when compared to the control. Further detailed investigation on activation of these enzymes, by considering other ranges of thermal treatments, tracking enzyme activity, can lead to promising results. The highest reduction in oil content compared to the control was 8.8%.

5.1.5.4 Sonication (D)

D-1 - Samples pre-treated with Ca^{+2}, much like in pre-treatment A, combined with sonication pre-treatment (D) resulted in a further decrease of oil absorption. The highest reduction in oil content compared to the control was 30.2%.

D-2 - Samples that were heat-treated (C) and undergone the combination of pre-treatments (A) and (D) altogether showed the lowest values ($p < 0.5$) for oil absorption. The positive effect of each pre-treatment (A, C, and D) to lower oil absorption in the final product could be verified in this preliminary experiment. It reiterates the more reason to explore different directions, as discussed in the items above, for studies in this area. The highest reduction in oil content compared to the control was 14.9%.

Table 5.7 summarizes the best results achieved for oil-absorption reduction in this preliminary study for the pre-treatments A, B, C, and D.

Table 5. 7. Highest Oil-absorption reduction for the pre-treatments A, B, C, and D.

Pre-treatment	**Lowest Oil content [g oil/g D.M.]**	**Reduction [%]**
A ($CaCl_2$ 20000 ppm / 30 min)	0.227 ± 0.005	26.5
B (EtOH 70% + $CaCl_2$ 10000 ppm / 2 min)	0.273 ± 0.014	19.0
C (Heat + $CaCl_2$ 10000 ppm / 60 min)	0.270 ± 0.005	8.8
D-1 ($CaCl_2$ 20000 ppm / sonicated / 30 min)	0.220 ± 0.001	**30.2**
D-2 (Heat + Sonication + $CaCl_2$ 10000 ppm / 60 min)	0.252 ± 0.014	14.9

Due to all these considerations, it was decided that the investigation of the effect of structure stabilization of the potato cellular tissue prior to deep-fat frying on the final oil content of potato chips, would result in valuable information for scientists and the food industry. The use of Ca^{+2} ions assisted with sonication to improve calcium impregnation in the tissue, can promote cellular structure stabilization prior to frying. The evaluation of different concentrations, soaking periods, and sonication treatments is evaluated in more detail in the following sections.

5.2. Mass transfer during calcium chloride soaking pre-treatments

Figure 5.6 shows the mass gain to and loss from the potato slices undergoing the calcium chloride treatment at 0, 1, 5, 10, 20, and 50 x 10^3 ppm, under 30 minutes of sonication (sonicated), and 30 minutes without sonication processing (non-sonicated).

All the experiments were conducted in ice water. The temperature mapping of the bath is presented in the next section.

Both processes, sonication and non-sonication, showed mass gain in the samples at lower concentrations of calcium chloride. This was noticed by the touch during the experiment (the samples became very rigid). The mass of fluid gain was due to the lower concentration of $CaCl_2$ in the solution. The difference in osmotic pressure between the sample and solution resulted in fluid transfer to the potato tissue (higher osmotic pressure), thus an increase of the cellular turgor pressure of tissue resulted. Turgor pressure is defined by the pressure exerted by fluid in a cell that presses the cell membrane against the cell wall of the plant tissue. Conversely, at higher concentrations of the calcium chloride solution, the samples experience mass losses. At the concentration of 20×10^3 ppm of calcium chloride, it was difficult to notice if the samples were more rigid or less rigid as they were similar to the samples before undergoing any treatment. However, at 50×10^3 ppm of calcium chloride, it was evident that they became very leathery. The higher concentration of solutes in the calcium chloride solution had higher osmotic pressure when compared to the potato tissue. Consequently, a difference of osmotic pressure caused mass loss of the potato to the calcium chloride solution, thus resulting in a pliable slice.

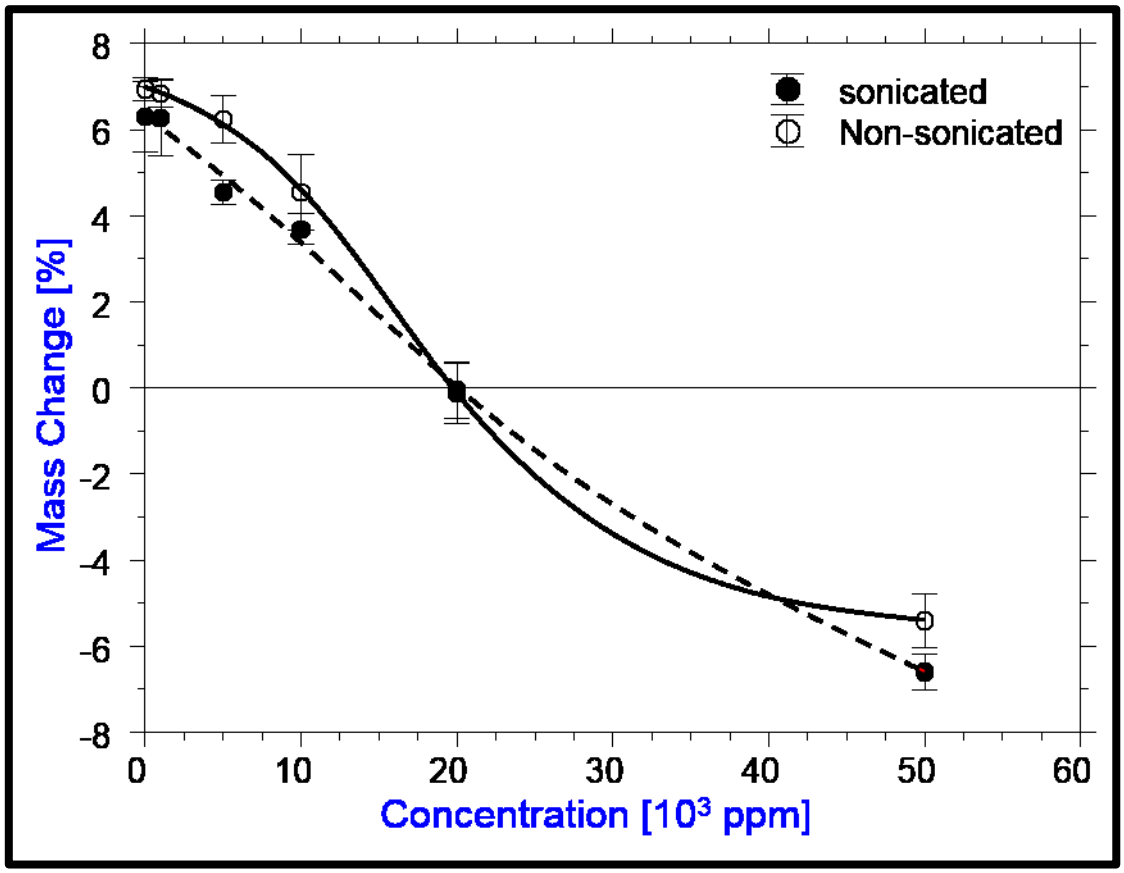


Figure 5. 6. Mass transfer at various concentrations of calcium chloride (markers are experimental data and lines are curve fitting with the Logistic model).

5.2.1 Mass transfer parameter-fitting estimation for the non-sonication process

Three different models were considered to fit the experimental data: linear, quadratic, and logistic. Figure 5.7 shows the plots for the non-sonicated and sonicated data and curve fitting for the 3 different models. It is clear from the data that the best fit was obtained with the logistic model for both set of experiments. The quadratic model, a simpler model than the logistic, predicted the sonicated data better than the non-sonicated experiment, however the linear model fail to fit any of the experimental data.

Therefore, the 4-parameter logistic model having an upper and lower asymptote was chosen for the best fit according to the "fit statistics for comparing multiple models" platform using the statistics software JMP Pro 13.1.0. Tables 5.8 and 5.9 show the model comparison report with the fit statistics parameters considered. They were: AICc, AICc Weight, BIC, SSE, MSE, RMSE, and R-Square. Their specific definition can be found on the section 4.13.1 (Statistical data analysis and figure plots).

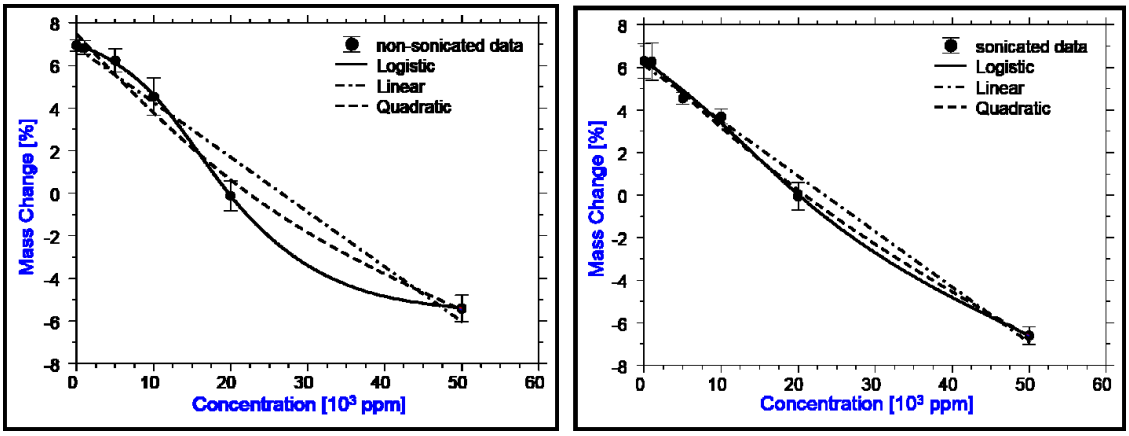


Figure 5. 7. Sonicated and non-sonicated data as a function of calcium chloride concentration fitted with different models.

Table 5. 8. Statistic parameters for model comparisons (non-sonicated).

Model	AICc	AICc Weight	BIC	SSE	MSE	RMSE	R^2
Logistic 4P	91.7287	0.9999	99.5160	15.1809	0.3530	0.5941	0.9847
Quadratic	122.1299	2.503×10^{-7}	128.5781	30.5786	0.6949	0.8336	0.9691
Linear	142.0190	1.201×10^{-11}	147.0113	49.1274	1.0917	1.0449	0.9503

Table 5. 9. Statistic parameters for model comparisons (sonicated).

Model	AICc	AICc Weight	BIC	SSE	MSE	RMSE	R^2
Logistic 4P	91.3007	0.4553	98.4851	16.0599	0.4118	0.6417	0.9820
Quadratic	90.9606	0.5397	96.9527	16.9143	0.4229	0.6503	0.9810
Linear	100.3023	0.0051	104.9705	22.2444	0.5425	0.7366	0.9750

The AICc weight (normalized AICc) can be interpreted as the probability that a particular model is the true model given that one of the fitted models is the truth. Therefore, the model with the AICc weight closest to one is the better fit among them. In this study, the Logistic 4P model is clearly the better fit.

Equation (5.1) presents the logistic model used in this study, where ΔM represents the % of mass gain (positive values) or loss (negative values). Its parameters are shown on Table 5.10.

$$\Delta M(\%) = d + \frac{a - d}{1 + e^{b(C-f)}} \quad 5.1$$

where: b is curve slope, f is the inflection point, a is the lower asymptote, d is the upper asymptote; and C is the concentration [10^3 ppm].

The linear model (Eq 5.2) and the quadratic model (Eq. 5.3) curve fitting parameters are shown in Table 5.11 for the non-sonicated experiments:

$$\Delta M(\%) = a + bC \quad 5.2$$

where a and b are the intercept and the slope, respectively, and C is the concentration [10^3 ppm].

$$\Delta M(\%) = a + bC + dC^2 \quad 5.3$$

where a, b, and d are the intercept, slope and quadratic terms, respectively, and C is the concentration [10^3 ppm].

Table 5. 10. Parameter estimates for the logistic model (non-sonicated).

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Curve Slope (b)	-0.153323	0.0166	-0.1859	-0.1206
Inflection Point (f)	17.416629	0.6089	16.2230	18.6102
Lower Asymptote (a)	-5.499876	0.2260	-5.9430	-5.0567
Upper Asymptote (d)	7.855967	0.4219	7.0289	8.6830

Table 5. 11. Parameter estimates for the linear and quadratic models (non-sonicated).

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Linear model				
Intercept (a)	6.8623232	0.1992359	6.4718281	7.2528183
Slope (b)	-0.257638	0.008779	-0.274845	-0.240432
Quadratic model				
Intercept	7.4956555	0.2007424	7.1022076	7.8891035
Slope	-0.399243	0.0282904	-0.454691	-0.343794
Quadratic	0.0027891	0.0005399	0.001731	0.0038472

5.2.2 Mass transfer parameter-fitting estimation for the sonicated process

Three different models were considered to fit the experimental data: linear, quadratic, and logistic. The 4-parameter logistic model ($R^2 = 0.9820$) having an upper and lower asymptote was chosen for the best fit according to the "fit statistics for comparing multiple models" platform using the statistics software JMP Pro 13.1.0.

The parameters for the logistic model used in this study are shown on Table 5.12. Table 5.13 have the results for the linear and quadratic models.

Table 5. 12. Parameter estimates for the logistic model (sonicated).

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Curve Slope (b)	-0.070266	0.0239	-0.1171	-0.0234
Inflection Point (f)	15.744156	3.5780	8.7315	22.7568
Lower Asymptote (a)	-8.200577	1.3372	-10.8214	-5.5798
Upper Asymptote (d)	11.120606	3.4634	4.3325	17.9087

Table 5. 13. Parameter estimates for the linear and quadratic models (sonicated).

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Linear model				
Intercept (a)	6.1189227	0.1432483	5.8381613	6.3996841
Slope (b)	-0.260634	0.0065121	-0.273397	-0.24787
Slope	-0.343179	0.0239503	-0.390121	-0.296237
Quadratic	0.0016323	0.0004598	0.0007312	0.0025335

Table 5.13. Continued

Parameter	Estimate	Std Error	Lower 95%	Upper 95%
Quadratic model				
Intercept	6.4559036	0.1581206	6.1459929	6.7658144
Slope	-0.343179	0.0239503	-0.390121	-0.296237
Quadratic	0.0016323	0.0004598	0.0007312	0.0025335

5.2.3 Point of Inflection – Sonicated and Non-Sonicated processes

In this study, the point of inflection was used as a predictor for the calcium solution concentration where there should not be gain or loss of mass during that specific processing time. In other words, it would be the concentration where the osmotic pressure of the solution and the samples would be equal. Tables 5.10 and 5.11 show the point of inflection for both processes. It can be observed that this will happen at a lower concentration of calcium chloride on the sonication process (f =15.7 x 10^3 ppm) than in the non-sonication process (f = 17.4 x 10^3 ppm). Both estimated values were close to the experimental concentration of 20.0 x 10^3 ppm of calcium chloride where the texture (by the touch) of the samples after treatment were similar to the samples that did not undergone the calcium chloride treatment. A two-way factorial ANOVA to investigate the effects of concentration levels and sonication (S) and non-sonication (NS) processes on mass transfer was performed (Table 5.14).

Table 5. 14. Two-Way Factorial ANOVA for the effects of calcium chloride concentration and sonication (S)/Non-sonication (NS) on mass transfer.

Factors	DF	Sum of Squares	F Ratio	Prob > F
Concentration	5	1837.4367	996.2128	<0.0001*
S/NS	1	14.7197	39.9033	<0.0001*
Concentration*S/NS	5	6.5376	3.5445	0.0061*

The effect of both main variables (concentration, and sonication) was significant ($p < 0.05$) indicating that the mass transfer responses in the population differs as a function of calcium chloride concentration and sonication/non-sonication. This test also showed a statistically significance ($p < 0.05$) between the interactions of both main effects, indicating that the effect of sonication differs for different concentrations.

In this study, the non-sonicated samples would have an estimated osmotic-pressure equilibrium at 17. 4 x 10^3 ppm concentration ($CaCl_2$). Under the ultrasound wave treatment, the estimated equilibrium osmotic pressure would be brought down to a concentration of 15.7 x 10^3 ppm ($CaCl_2$). It can be suggested that when sonication is used the samples will start losing mass sooner than the non-sonicated samples and they will experience lower turgor pressures than the non-sonicated ones. Higher turgor pressure would facilitate cell de-attachment.

5.3. Assessment of temperature distribution in the sonicator tank

The first challenge during the experiments was how to maintain the temperature of the potato slices the same and uniform for the sonication and non-sonication

treatments. Figure 5.8 shows the temperature distribution within the ultrasound tank at time 0 minutes.

During the sonication process, part of the energy used by the piezoelectric transducers to generate the ultrasound waves is converted to heat, and usually a considerably temperature increase can be observed at certain conditions, such as duration of the sonication, power and frequency of the sonicator, design of the transducers, and cooler mechanism, media volume, media viscosity, etc. Paying attention to all these factors to assure consistency fundamental to obtain a reproducible process.

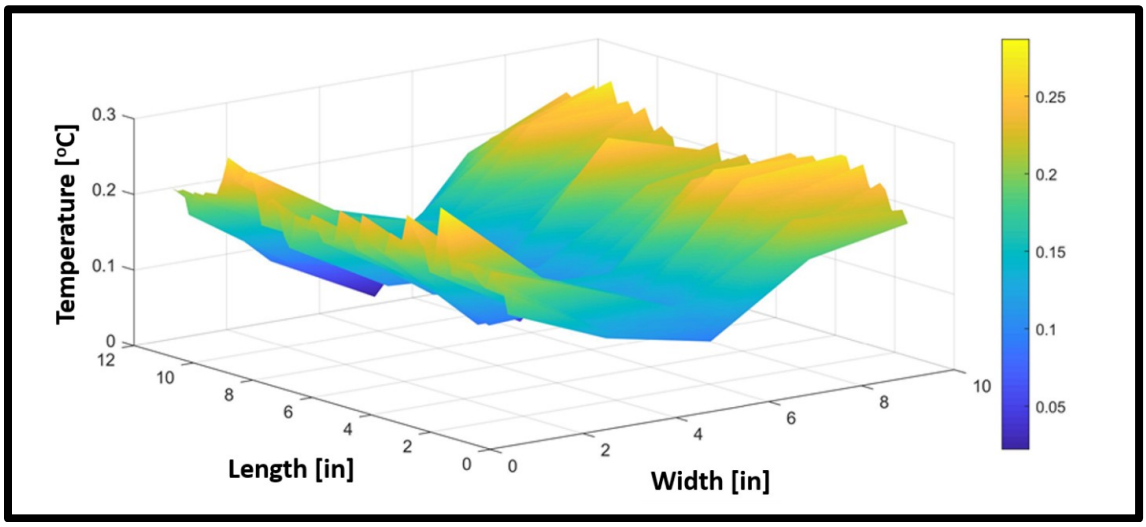


Figure 5. 8. Temperature distribution within the ultrasound tank at time 0 minutes.

The second challenge was to make sure that the temperature of the samples on the sonication process would not rise considerably during the treatment, so sonicated and

non-sonicated samples could be compared. Figure 5.9 shows the temperature distribution within the ultrasound tank after 30 minutes of ultrasound operation.

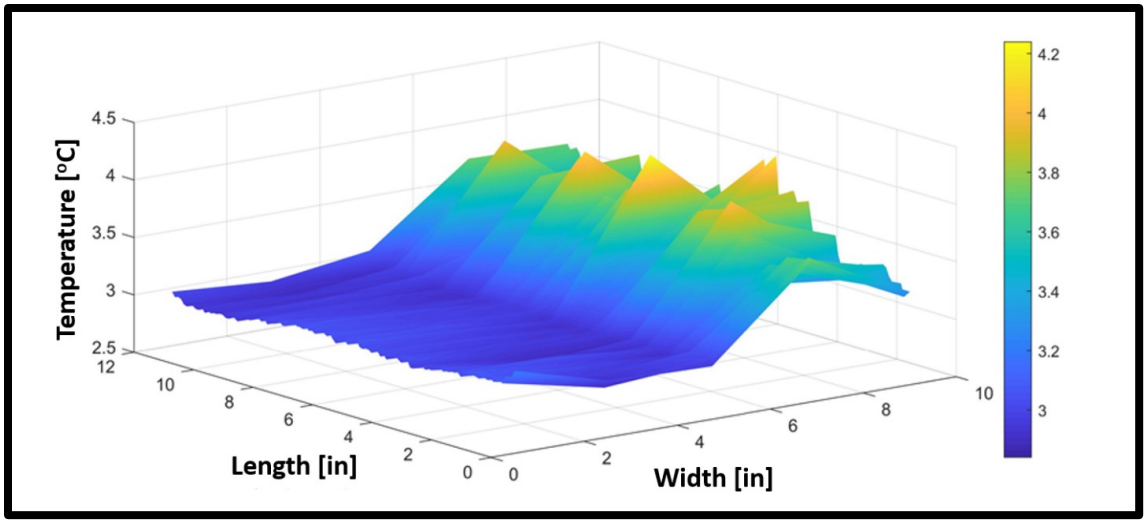


Figure 5. 9. Temperature distribution within the ultrasound tank after 30 minutes of ultrasound operation.

The initial processing temperature distribution (Figure 5.8), remained about the same throughout the whole process for the non-sonicated samples (30 minutes). There was a little temperature buildup close to the walls of the bath, probably due to the temperature difference between the walls and the outside ambient (21.0 ºC – recorded on a VWR® general-purpose alcohol-in-glass thermometer 1ºC scale resolution). Nevertheless, the minimum temperature recorded on the bath was of T_{min} = 0.02225ºC and the maximum was of T_{max} = 0.28664 ºC. Therefore, a maximum difference of temperature of ΔT = 0.26439ºC can be considered negligible for this purpose.

The final processing temperature distribution, after 30 minutes of sonication operation, is represented by Figure 5.9. It can be observed that a temperature along the length of one of the side-walls of the bath was more pronounced than in any other part of bath. One explanation for it is that probably a heat sink is situated in that part of the bath. The ultrasound bath's manual did not have the blueprint of the equipment. Nevertheless, the minimum temperature recorded on the bath after 30 minutes of operation, was of $T_{min} = 2.84052$ºC and the maximum was of $T_{max} = 4.24192$ºC. Therefore, a maximum difference of temperature of $\Delta T = 1.40140$ºC can be considered negligible for this purpose as well.

Comparing the $T_{min} = 0.02225$ºC, at time equal 0 minutes, and $T_{max} = 4.24192$ºC, at time equal 30 minutes, a potential maximum $\Delta T_{max} = 4.21967$ºC temperature increase could be observed in some point within the bath during the 30 minutes of operation.

5.4. Pre-treatments

5.4.1 Optimization of pre-treatment for potato chips oil content using response surface

5.4.1.1 Optimization design and desirability function

The pre-treatment optimum operation conditions were investigated with the goal of minimizing oil uptake in potato chips. The effect of ultrasound waves, time, and calcium chloride concentration on the final oil content of deep-fat fried potato chips was evaluated. Response surface methodology (RSM) was used to evaluate the results of the central composite design (CCD) for the oil content response as a function of time (3 levels), calcium chloride concentration (5 levels) and the use of sonication or non-

sonication (2 levels). A statistical model representing the influence of those factors (time, concentration, sonication or non-sonication) on the response dependent variable (oil content of the potato chips) was developed and validated using analysis of variance (ANOVA).

5.4.1.2 Experimental design

A Central composite of RSM for a three-variable experimental design was carried out. The independent factors considered were bath time (X_1: 5, 10, 30 minutes), calcium chloride concentration (X_2: 1.0, 5.0, 10.0, 20.0, and 50.0 x 10^3 ppm), and sonication or lack of thereof (X_3: S/NS). The only dependent variable was the oil content of the potato chips in dry basis. This resulted on a Factorial 3x5x2 design, therefore 30 data for the response variable were inputted, and each came from an average observation of 3 replicates measured analytically.

The results of the pre-treatment independent variables for the response variable oil content, according to the corresponding combination of the independent variables and their levels were used to run the CCD analysis (Table 5.15).

The models constructed for the RSM included the main factors (X_1, X_2, X_3), quadratic (X_1*X_1, X_2*X_2, X_3*X_3), and their cross-product (X_1*X_2, X_1*X_3, X_2*X_3).

Three different case-models were used to obtain the desirability functions. The first (1) included all main factors (X_1, X_2, X_3). The second (2) and the third (3) model did not include the X_3 term, two analyses were carried out separating the responses for the non-sonicated samples, and sonicated one, respectively. For all three models, their individual main factors as well as their quadratic and cross-product terms, were

included. Figure 5.10 shows the three cases at the optimum conditions for minimum oil uptake.

A summary of fit and ANOVA for the regression models of the dependent variable oil content of potato chips are represented on Table 5.16.

Table 5. 15. The 3x5x2 Factorial design and response variable data.

X_1 [min]	X_2 [10^3 ppm]	X_3	Oil content [d.b.]
5	10	S	0.291
30	10	NS	0.302
30	5	NS	0.316
30	1	S	0.277
30	20	NS	0.292
5	1	S	0.301
10	10	S	0.278
10	20	S	0.228
5	20	NS	0.287
30	1	NS	0.29
10	10	NS	0.29
5	50	S	0.295
10	5	NS	0.299
5	1	NS	0.293
5	50	NS	0.21
5	5	S	0.295
30	5	S	0.321
10	1	S	0.295
10	20	NS	0.279
10	50	S	0.184
30	50	S	0.172

Table 5.15. Continued

X_1 [min]	X_2 [10^3 ppm]	X_3	Oil content [d.b.]
10	5	S	0.291
5	20	S	0.243
30	10	S	0.301
10	1	NS	0.296
30	50	NS	0.22
10	50	NS	0.215
30	20	S	0.237
5	10	NS	0.31
5	5	NS	0.304

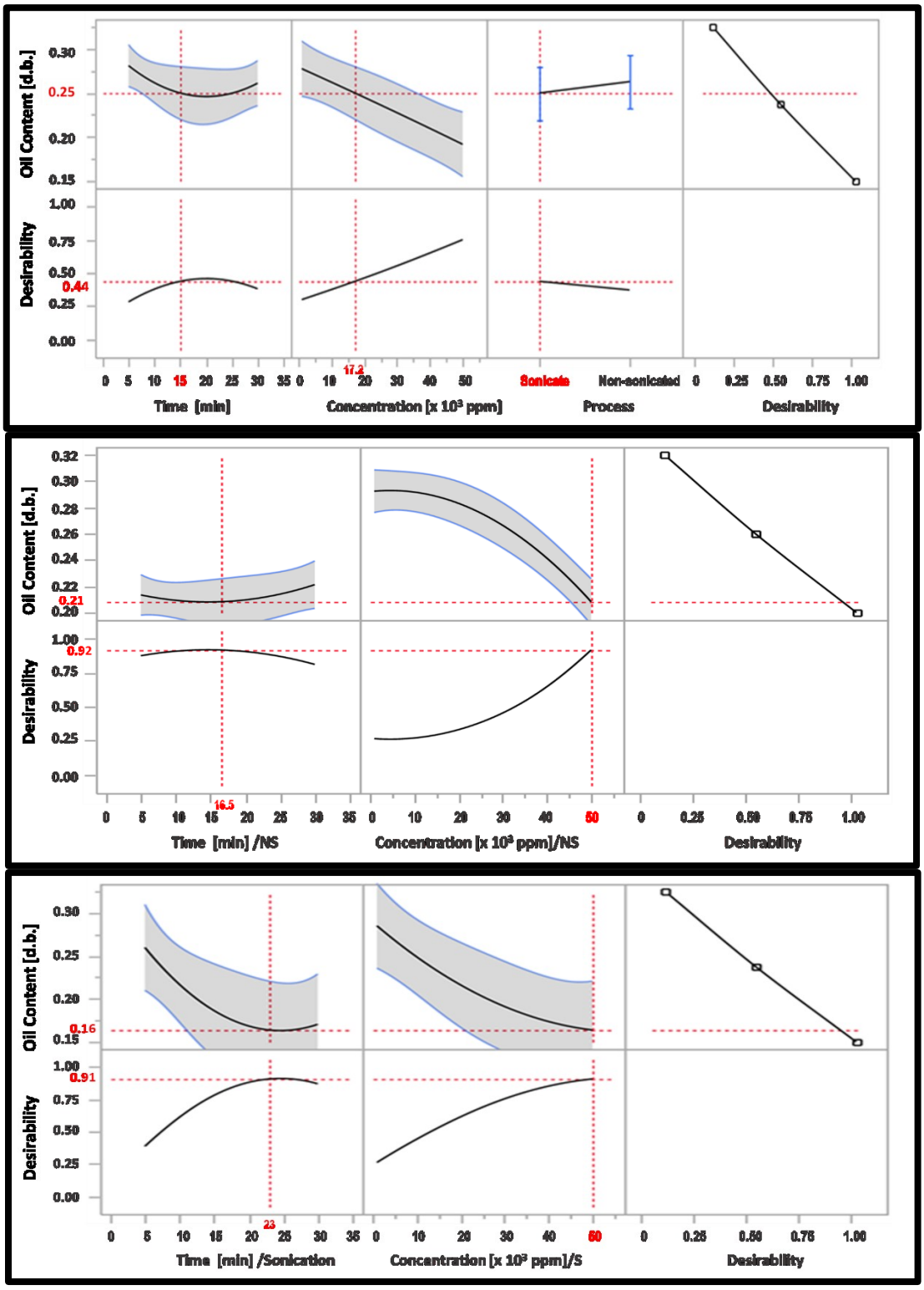


Figure 5. 10. Desirability functions for case 1 (top), case 2 (middle), and case 3 (bottom).

Table 5. 16. Analysis of variance and fit statistics for the models.

	ANOVA (model)				Summary of fit	
Factors	DF	Mean-Sq.	F value	Prob > F	RMSE	R^2
X_1, X_2, X_3	8	0.0043	7.4911	0.0001*	0.0239	0.7405
X_1, X_2 (NS)	5	0.0033	47.4104	< 0.0001*	0.0084	0.9634
X_1, X_2 (S)	5	0.0043	5.7891	0.0115*	0.0271	0.7628

Case 1 – (X_1, X_2, X_3)

The optimized results would be a pre-treatment of the potato chips in a calcium chloride solution with a concentration of 17.2 x10^3 ppm for 15 minutes. The expected oil content would be 0.25 kg oil/kg DM. The preferred treatment would be the sonication.

Case 2 – (X_1, X_2 – Non-sonicated treatment only)

The optimized results would be a pre-treatment of the potato chips in a calcium chloride solution with a concentration of 50 x10^3 ppm for 16.5 minutes. The expected oil content would be 0.21 kg oil/kg D.M.

Case 3 – (X_1, X_2 – Sonicated treatment only)

The optimized results would be a pre-treatment of the potato chips in a calcium chloride solution with a concentration of 50 x10^3 ppm for 23 minutes. The expected oil content would be 0.16 kg oil/kg D.M.

Since case (1) showed a relatively low value for the model R^2 (0.74), an attempt to improve the determination coefficient was made. Separating the sonicated and non-sonicated factors in two different cases, resulted in $R^2 = 0.96$ and $R^2 = 0.76$ for cases (2) and (3), respectively.

Results from CCD analysis (Table 5.17) showed that the linear regression coefficient of time was negative for the oil content response for the sonicated (S) and non-sonicated (NS) treatments. This result indicates that the longer the samples stay in the pre-treatment, the lower be the oil uptake during frying. The significant negative linear regression coefficients for $CaCl_2$ concentration (-1.753×10^{-6}) (sonicated and non-sonicated – Case 1), (-1.04110^{-6}) (non- sonicated - Case 2), (-2.465×10^{-6}) (sonicated – Case 3), and the significant quadratic term for $CaCl_2$ concentration (-4.11×10^{-11}) (non-sonicated), indicate that the oil uptake by the chips during frying will decrease with the increase of concentration of $CaCl_2$. The significant quadratic coefficient (-4.11×10^{-11}) (non-sonicated – Case 2) of $CaCl_2$ concentration indicates the existence of a curvature in the response surface.

The response surface plots for the model in case-2 (non-sonicated) and case-3 (sonicated), is shown on Figure 5.11.

Table 5. 17. Parameter estimates of the central composite design (CCD) analysis.

Term (Case 1) – Sonicated and Non-sonicated	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	0.3039924	0.008834	34.41	<.0001*
Time	-0.001173	0.000749	-1.57	0.1321
Conc	-1.753×10^{-6}	4.512×10^{-7}	-3.89	0.0009*
S/SN[Son]	-0.006467	0.004366	-1.48	0.1534
(Time-15)*(Time-15)	0.0001538	0.000098	1.57	0.1316
(Time-15)*(Conc-17200)	-3.742×10^{-8}	2.298×10^{-8}	-1.63	0.1183
(Conc-17200)*(Conc-17200)	-1.47×10^{-12}	2.02×10^{-11}	-0.07	0.9428
(Time-15)*S/SN[Son]	-0.000393	0.000404	-0.97	0.3421
(Conc-17200)*S/SN[Son]	2.7024×10^{-8}	2.482×10^{-7}	0.11	0.9143
Term (Case 2) – Non-sonicated	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	0.3065405	0.004363	70.26	<.0001*
Time NonS	-0.000154	0.00037	-0.42	0.6868
Conc NonS	-1.04110^{-6}	2.228×10^{-7}	-4.67	0.0012*
(Time NonS-15)*(Time NonS-15)	0.0000564	4.841×10^{-5}	1.17	0.2739
(Time NonS-15)*(Conc NonS-17200)	5.6097×10^{-9}	1.135×10^{-8}	0.49	0.6330
(Conc NonS-17200)*(Conc NonS-17200)	-4.11×10^{-11}	9.97×10^{-12}	-4.12	0.0026*
Term (Case 3) – Sonicated	**Estimate**	**Std Error**	**t Ratio**	**Prob>|t|**
Intercept	0.3014443	0.014157	21.29	<.0001*
Time Son	-0.002192	0.0012	-1.83	0.1009
Conc Son	-2.465×10^{-6}	7.23×10^{-7}	-3.41	0.0077*
(Time Son-15)*(Time Son-15)	0.0002512	0.000157	1.60	0.1442
(Time Son-15)*(Conc Son-17200)	-8.046×10^{-8}	3.683×10^{-8}	-2.18	0.0567
(Conc Son-17200)*(Conc Son-17200)	3.815×10^{-11}	3.23×10^{-11}	1.18	0.2685

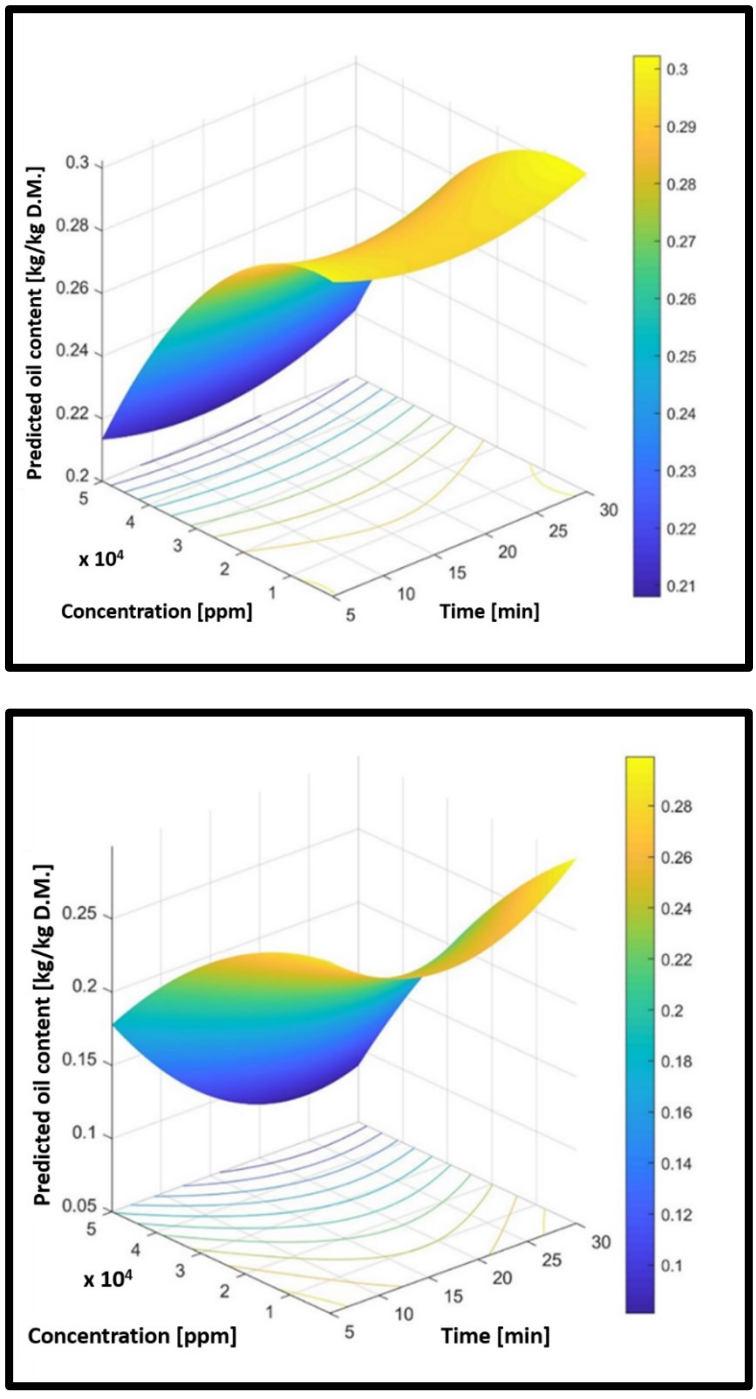


Figure 5. 11. Response surface plots of oil uptake (kg oil/kg D.M.) in potato chips under the non-sonicated pre-treatment (top) and under the Sonicated pre-treatment (bottom).

The values for oil content (kg oil/kg D.M.) of fried potato chips after being pre-treated by sonication and non-sonication are shown in Table 5.18. Control samples (potatoes not pre-treated) showed an oil content of 0.303 ± 0.012 kg oil/kg D.M.

Table 5. 18. Oil content (kg oil/kg D.M.) of pre-treated and fried potato chips.

Non-sonicated pre-treated			
Concentration of $CaCl_2$ [10^3ppm]	**Time (minutes)**		
	5	10	30
1	$_{x}$ 0.293 ± 0.014 ^{a}	$_{x}$ 0.296 ± 0.008 ^{a}	$_{x}$ 0.290 ± 0.012 ^{b}
5	$_{x}$ 0.304 ± 0.027 ^{a}	$_{x}$0.299 ± 0.015 ^{a}	$_{x}$ 0.316 ± 0.010 ^{a}
10	$_{x}$ 0.310 ± 0.006 ^{a}	$_{y}$ 0.290 ± 0.006 ^{a}	$_{x,y}$ 0.302 ± 0.004 ^{b}
20	$_{x,y}$ 0.287 ± 0.003 ^{a}	$_{y}$ 0.279 ± 0.006 ^{a}	$_{x}$ 0.292 ± 0.005 ^{b}
50	$_{x}$ 0.210 ± 0.012 ^{b}	$_{x}$ 0.215 ± 0.013 ^{b}	$_{x}$ 0.220 ± 0.013 ^{c}
Sonicated pre-treated			
Concentration of $CaCl_2$ [10^3ppm]	**Time (minutes)**		
	5	10	30
1	$_{x}$ 0.301 ± 0.021 ^{a}	$_{x}$ 0.295 ± 0.01 ^{a}	$_{x}$ 0.277 ± 0.015 ^{a}
5	$_{x}$ 0.295 ± 0.018 ^{a}	$_{x}$ 0.291 ± 0.032 ^{a}	$_{x}$ 0.321 ± 0.026 ^{a}
10	$_{x,y}$ 0.291 ± 0.005 ^{a}	$_{y}$ 0.278 ± 0.013 ^{a}	$_{x}$ 0.301 ± 0.006 ^{a}
20	$_{x}$ 0.243 ± 0.013 ^{b}	$_{x}$ 0.228 ± 0.006 ^{b}	$_{x}$ 0.237 ± 0.012 ^{b}
50	$_{x}$ 0.197 ± 0.011 ^{c}	$_{x}$ 0.184 ± 0.014 ^{b}	$_{x}$ 0.172 ± 0.018 ^{c}

Mean values ± standard deviations followed by different letters within the same column^{a-c} and different letters within the same row^{x-z} for each response are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test.

For the sonicated pre-treated samples, statistical significance ($p < 0.05$) of the response started at the calcium chloride concentration of 20 x 10^3 ppm at all times evaluated. For the non-sonicated treatment, significant changes ($p < 0.05$) in the response only started after 30 minutes of pre-treatment.

As for the factor "time", it appears that its effect on the response is not statistically significant ($p > 0.05$) at any concentration of calcium chloride evaluated in this experiment for both pre-treatments.

The difference Student's t test was performed to evaluate differences on the responses between sonicated (S) and non-sonicated (NS) pre-treated samples at 50 x 10^3 ppm at all times evaluated (Table 5.19).

Table 5. 19. Oil content (kg oil/kg D.M.) comparison between non-sonicated and sonicated pre-treated potato chip samples at the concentration of 50 x 10^3 ppm of $CaCl_2$.

$CaCl_2$ [50 x 10^3 ppm]	**Time [minutes]**		
	5	10	30
Non-sonicated	0.210 ± 0.012^a	0.215 ± 0.013^a	0.220 ± 0.013^a
Sonicated	0.197 ± 0.011^a	0.184 ± 0.014^a	0.172 ± 0.018^b

Mean values ± standard deviations followed by different letters within the same column for each response are significantly different ($p < 0.05$) according to the difference Student's t test ($\alpha = 0.05$).

At 50 x 10^3 ppm of calcium chloride, only at 30 minutes of pre-treatment a statistical significance ($p < 0.05$) can be observed between the non-sonicated and sonicated samples. The sonicated pre-treated samples showed the lower values.

Subsequently, another difference Student's t test was performed to evaluate differences on the responses between sonicated (S) and non-sonicated (NS) pre-treated samples at 30minutes at all concentration levels evaluated (Table 5.20).

Table 5. 20. Oil content (kg oil/ kg D.M.) comparison between Non-sonicated and Sonicated pre-treated potato chip samples at 30 minutes duration of pre-treatment.

$CaCl_2$ [10^3ppm]	**30 minutes**	
	Non-sonicated	**Sonicated**
1	0.290 ± 0.012 [a]	0.277 ± 0.015 [a]
5	0.316 ± 0.010 [a]	0.321 ± 0.026 [a]
10	0.302 ± 0.004 [a]	0.301 ± 0.006 [a]
20	0.292 ± 0.005 [a]	0.237 ± 0.012 [b]
50	0.220 ± 0.013 [a]	0.172 ± 0.018 [b]

Mean values ± standard deviations followed by different letters within the same row for each response are significantly different ($p < 0.05$) according to the difference Student's t test ($\alpha = 0.05$).

The first statistically significant difference on the response of the pre-treated samples at 30 minutes of duration is found at the concentration of 20 x 10^3 ppm of calcium chloride. The sonicated treatment showed lower values for oil content at 20 x 10^3 ppm (0.237 ± 0.012 kg oil/ g D.M.) and at 50 x 10^3 ppm (0.172 ± 0.018 kg oil/ g D.M.) $CaCl_2$ concentrations. When the samples were not pre-treated with ultrasound, values for the oil content were 23% and 28% higher at calcium chloride concentrations of 20 x 10^3 ppm and 50 x 10^3 ppm for 30 minutes, respectively. Compared with the

control, the sonicated-treated samples at 20 x 10^3 ppm and 50 x 10^3 ppm for 30 minutes, showed a decreased oil content in the chip by 22% and 43%, respectively.

Lower oil content of the potato chips can be achieved by treating the potato slices with higher concentrations of Ca^{+2}, however at the highest concentration (50 x 10^3 ppm) used in this study we noticed the adverse effect of bitterness caused by the chloride. Other sources of di-valent ions can be used as well. Calcium lactate, calcium propionate, and calcium gluconate have shown some of the benefits for product firmness improvement without the adverse effect of bitterness and off taste produced by calcium chloride (Hai-Ling Yang and Lawless, 2005).

Calcium concentration was reported to increase in fruit tissue using dipping technique regardless of the sources used, calcium lactate, calcium chlorine, and calcium propionate (Manganaris et al., 2007).

Another interesting source of calcium is the calcium-amino acid chelate. Formulations using it was patented as nutritionally functional chelates. Moreover, another material that can be used as source for di-valent ions is magnesium (Lester and Grusak, 1999).

One of the possible explanations for the lower oil content in the potato chips could be the stabilization of the middle lamellae and cell walls by the activation of the pectin-methylesterase (PME) enzyme (native in all higher plants), and readily availability of di-valent ions for formation of bridges between pectin molecules.

PME is a highly specific enzyme that removes methoxyl groups from pectin substances by hydrolyzing -$COOCH_3$ groups and leaving -COOH groups in place. In

turn, divalent cations such as Ca, Mg crosslink the chains, thereby preventing further degradation (Andersson et al., 1994). The result is a decrease of pectin solubility, more pronounced in the presence of calcium salts. Moreover, the presence of salts in general was found to enhance PME activity (Buren, 1973). PME activity observed at 25ºC is enhanced between 50 to 70ºC, but PME is rapidly inactivated at or above 70ºC (Bartolome and Hoff, 1972; Moledina et al., 1981; Ross et al., 2011).

The use of ultrasound waves to assist on the impregnation di-valent ions in the food-tissue may have a great influence on the structure of the final product. Calcium ions will assist in the formation of calcium-pectate bridges, thus firming the cell walls and increasing middle lamella-cell wall rigidity, preventing further degradation by the frying process. In theory, not only less pores would be formed (less rupture of cells), but also the chemical makeup of the formed pores would change with the ionic impregnation, consequently the surface tension would change as well, affecting the capillary pressure for oil pick-up.

In comparison with the non-sonicated treatment, it can be concluded that the application of ultrasound was effective in reducing the oil uptake of potato chips significantly. Perhaps the cavitation mechanism produced by the waves to the surface of the product, or even to the inner cells, was the main factor for better delivery of Ca^{+2} ions to parts of the cellular material where cross-polymerization of pectic substances would have taken place, thus impairing oil uptake.

Further research is needed to elucidate the exact mechanism of oil uptake as related to chemical composition and structure of the pores formed. Additionally, the

specific applicability of ultrasound waves as a delivery system for impregnation and structural changes of cellular matrices for other food systems needs to be evaluated.

5.5. Product quality attributes (PQA) and physical properties

Combinations of two-way factorial analyses of variance (ANOVA) were performed to evaluate the effect of the following factors on the various PQA and physical properties measured in this study:

- Effect of the calcium chloride concentrations at 2 levels (20 x 10^3 and 50 x 10^3 ppm);
- Effect of time in the calcium chloride bath at 2 levels (5 and 30 minutes);
- Effect of sonification and no-sonification (S/NS);

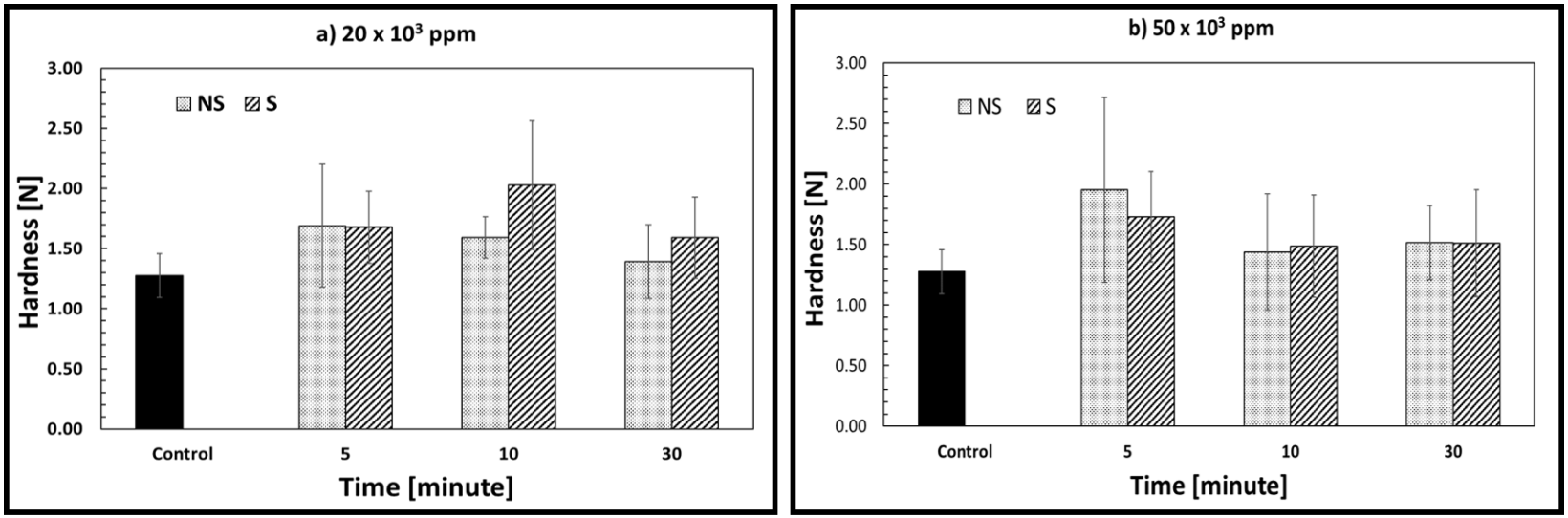
The effect of the interaction between the main factors on the various PQA and physical properties was also calculated.

The control represents the mean values for the potato chips that have not undergone any treatment.

5.5.1. Texture

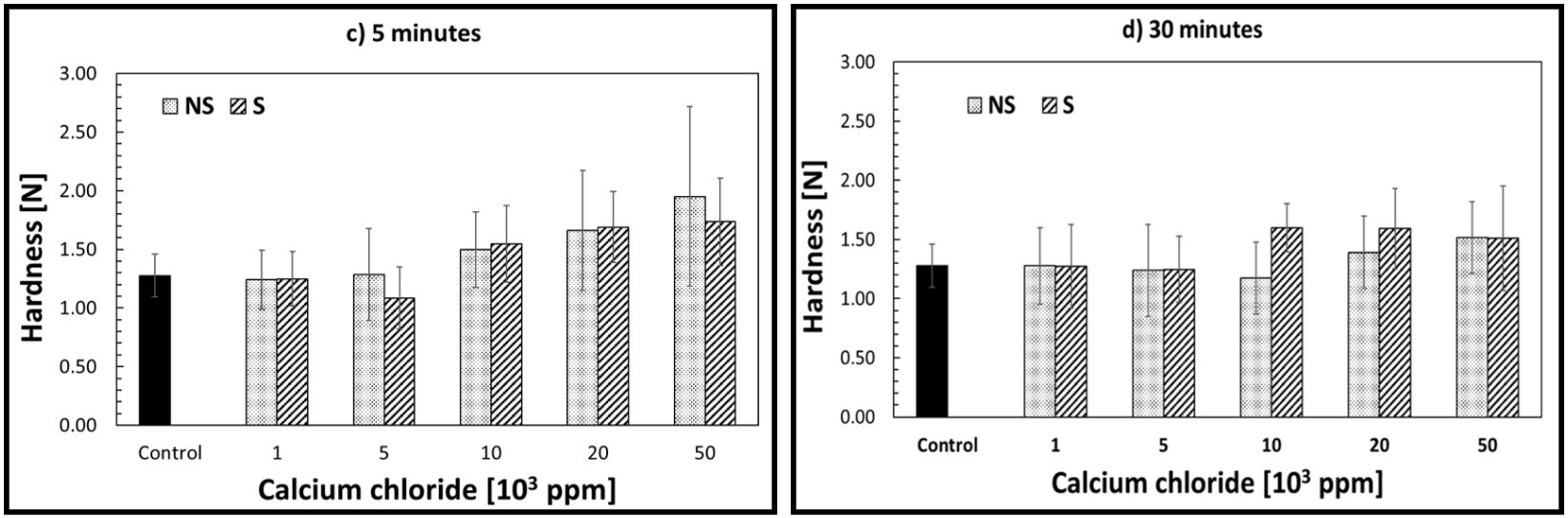
At a calcium chloride concentration of 20 x 10^3 ppm, there was a statistically significant ($p < 0.05$) effect of both main factors (S/NS, and time), indicating that the hardness responses in the samples change with S/NS and time. At $CaCl_2$ [50 x 10^3 ppm], only the factor "time" was significant ($p < 0.05$) (Figure 5.12). This test showed no evidence that a statistically significance ($p > 0.05$) for the interaction of both main factors exists at both concentrations.

At both treatment times, 5 and 30 minutes, there was a statistically significant ($p < 0.05$) effect of the main factor "concentration", indicating that the hardness responses in the samples change with concentration only. This test also showed no evidence that a statistically significance ($p > 0.05$) for the interaction of both main factors exists at both times (Figure 5.13).



Hardness [N]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	0.9329	6.0686	0.0158*	S/SN	1	0.0840	0.3543	0.5532
Time	2	1.46290	4.7582	0.0111*	Time	2	2.6814	5.6534	0.0049*
S/NS*Time	2	0.7205	2.3435	0.1023	S/SN*Time	2	0.3268	0.6890	0.5047

Figure 5. 12. Mean values and two-way ANOVA results for the texture parameter "Hardness" at $CaCl_2$ concentrations of 20 x 10^3 ppm (a), and 50 x 10^3 ppm (b).



Hardness [N]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	0.0890	0.5439	0.4620	S/NS	1	0.0001	0.0005	0.9830
Conc	4	10.3411	15.7867	<.0001*	Conc	4	1.8988	4.3129	0.0025*
S/NS*Conc	4	0.4816	0.7352	0.5694	S/NS*Conc	4	1.0686	2.4272	0.0505

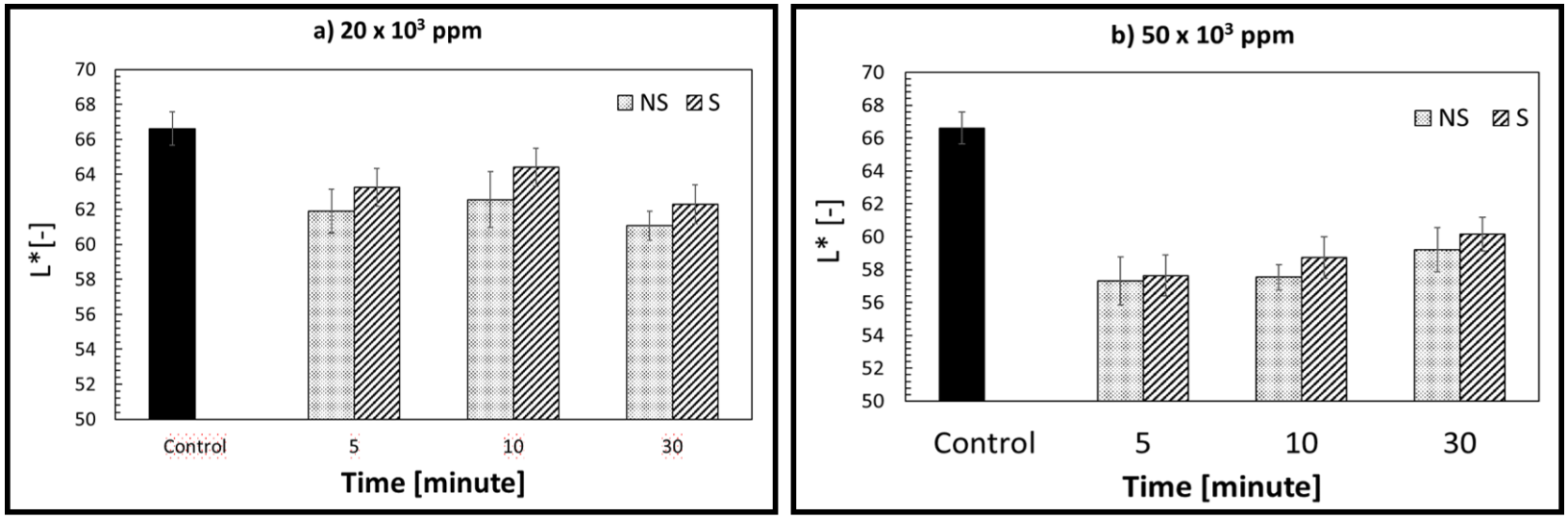
Figure 5. 13. Mean values and two-way ANOVA results for the texture parameter "Hardness" at time duration of 5 minutes (c) and 30 minutes (d).

5.5.2 Color

At a calcium chloride concentration of 20 x 10^3 ppm and 50 x 10^3 ppm, there was a statistically significant ($p < 0.05$) effect of both main factors (S/NS, and time), indicating that the color parameter "L*" responses in the samples change with S/NS, and time. This test also showed no evidence that a statistically significance ($p > 0.05$) for the interaction of both main factors exists (Figure 5.14).

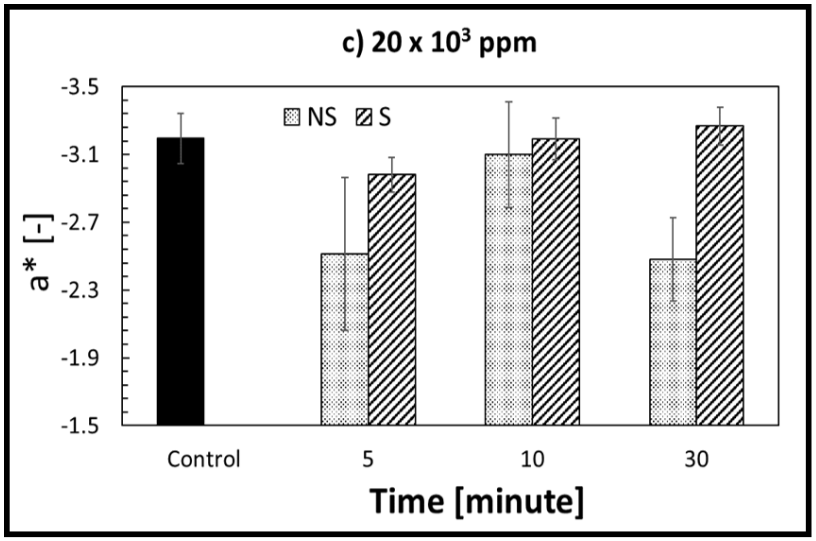
At a calcium chloride concentration of 20 x 10^3 ppm and 50 x 10^3 ppm, there was a statistically significant ($p < 0.05$) effect of both main factors (S/NS, and time), indicating that the color parameter "a*" responses in the samples change with S/NS and time. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists.

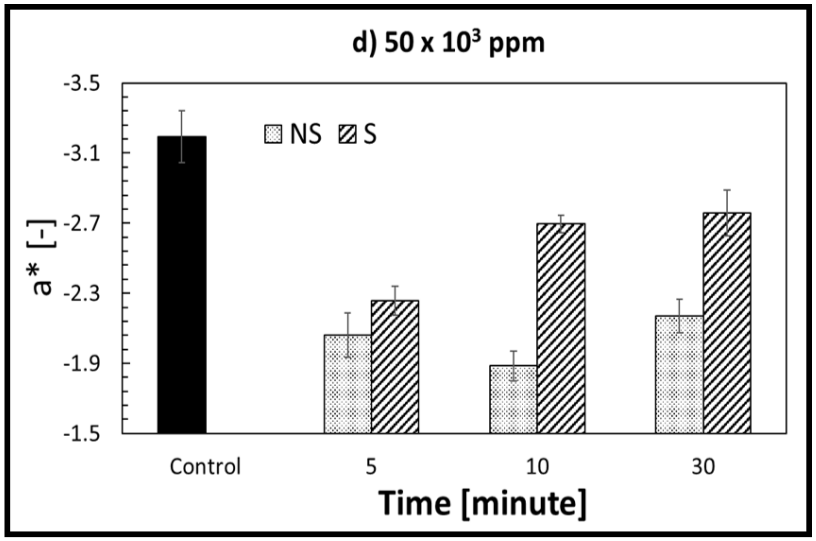
At a calcium chloride concentration of 20 x 10^3 ppm and 50 x 10^3 ppm, there was a statistically significant ($p < 0.05$) effect of both main factors (S/NS, and time), indicating that the color parameter "b*" responses in the samples change with S/NS and time. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists (Figure 5.16).



L*[-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	50.5455	35.4847	<.0001*	S/SN	1	16.2033	11.186	0.0012*
Time	2	49.1603	17.2561	<.0001*	Time	2	81.2518	28.047	<.0001*
S/NS*time	2	1.6253	0.5705	0.5674	S/SN*Time	2	3.1361	1.082	0.3431

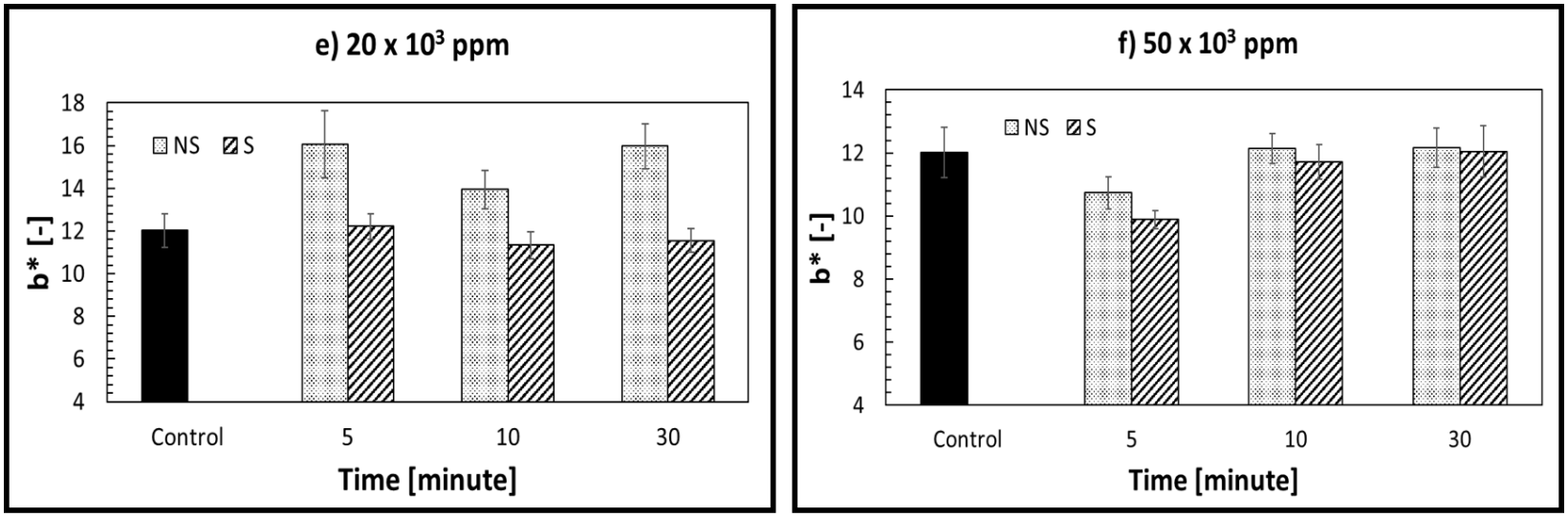
Figure 5. 14. Mean values and two-way ANOVA results for the color parameter "L*" at $CaCl_2$ concentrations of 20 x 10^3 ppm (a), and 50 x 10^3 ppm (b).





a* [-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	4.7241	70.3777	<.0001*	S/SN	1	6.3402	628.1571	<.0001*
Time	2	2.6022	19.3830	<.0001*	Time	2	1.4315	70.9130	<.0001*
S/NS*Time	2	1.9132	14.2510	<.0001*	S/SN*Time	2	1.4270	70.6933	<.0001*

Figure 5. 15. Mean values and two-way ANOVA results for the color parameter "a*" at $CaCl_2$ concentrations of 20 x 10^3 ppm (c), and 50 x 10^3 ppm (d).



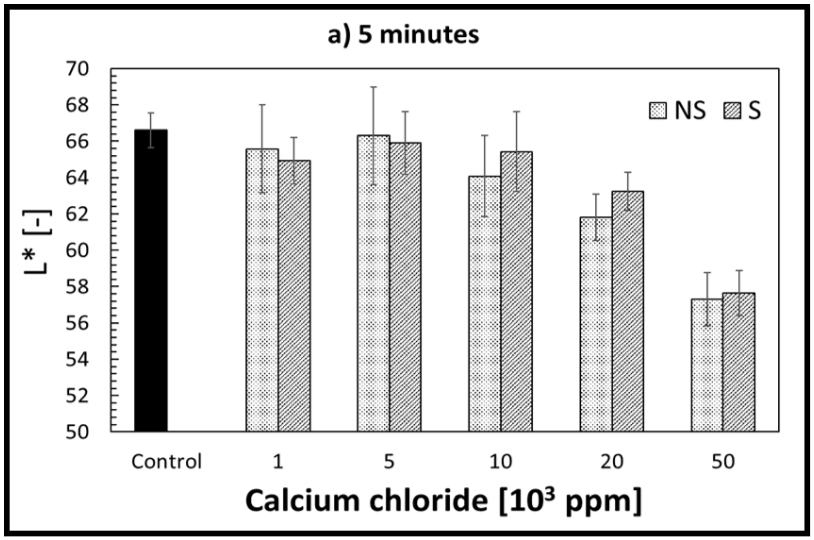
b [-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	308.4504	334.7745	<.0001*	S/SN	1	4.7652	14.5703	0.0003*
Time	2	39.0470	21.1897	<.0001*	Time	2	57.9049	88.5258	<.0001*
S/NS*Time	2	13.5246	7.3394	0.0011*	S/SN*Time	2	2.0520	3.1371	0.0487*

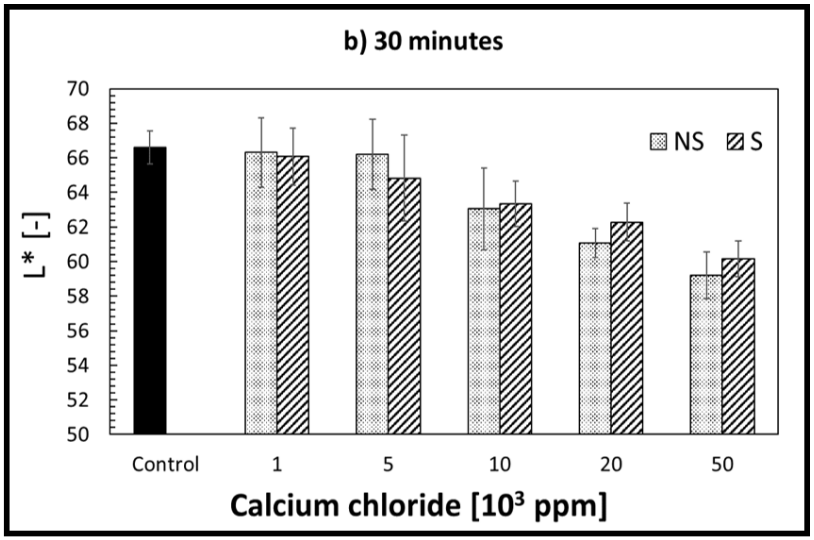
Figure 5. 16. Mean values and two-way ANOVA results for the color parameter "b*" at $CaCl_2$ concentrations of 20 x 10^3 ppm (e), and 50 x 10^3 ppm (f).

At both treatment times, 5 and 30 minutes, there was a statistically significant ($p < 0.05$) effect of the main factor "concentration", indicating that the color parameter "L*" responses in the samples change with concentration only. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at time = 30 minutes (Figure 5.17).

At both treatment times, 5 and 30 minutes, there was a statistically significant effect of both main factors (concentration, S/NS), indicating that the color parameter "a*" responses in the samples change with concentration and S/NS. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at both times, 5 and 30 minutes (Figure 5.18).

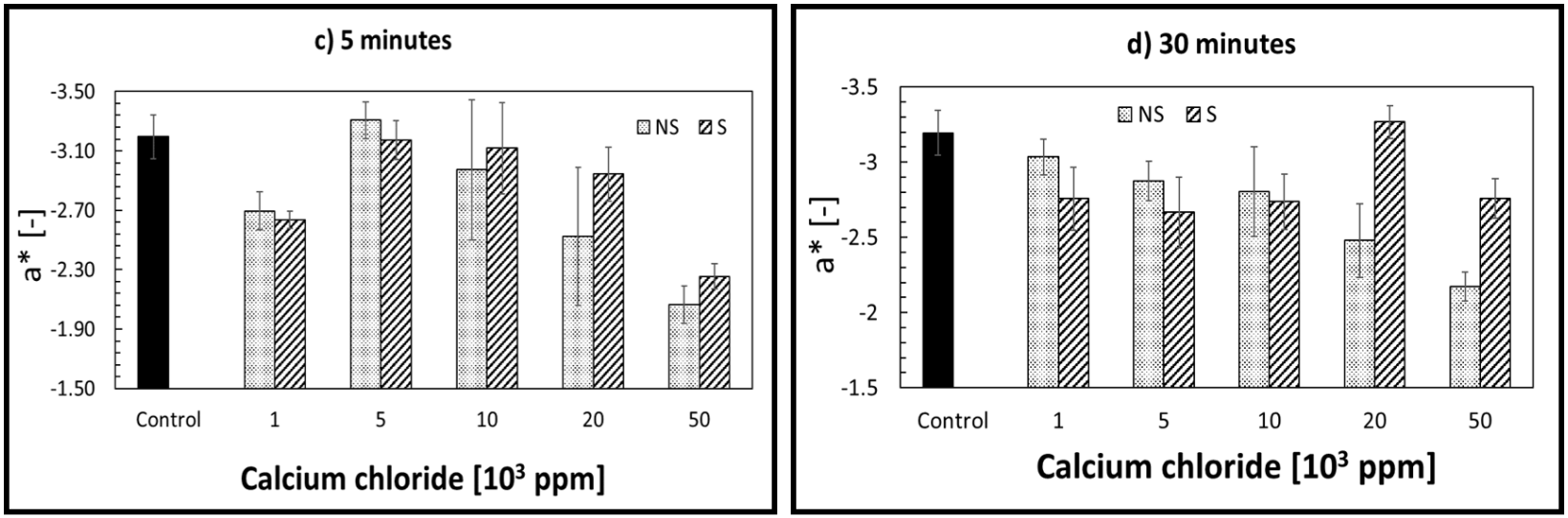
At both treatment times, 5 and 30 minutes, there was a statistically significant ($p < 0.05$) effect of both main factors (concentration, S/NS), indicating that the color parameter "b*" responses in the samples change with concentration and founds/NS. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at both times, 5 and 30 minutes (Figure 5.19).





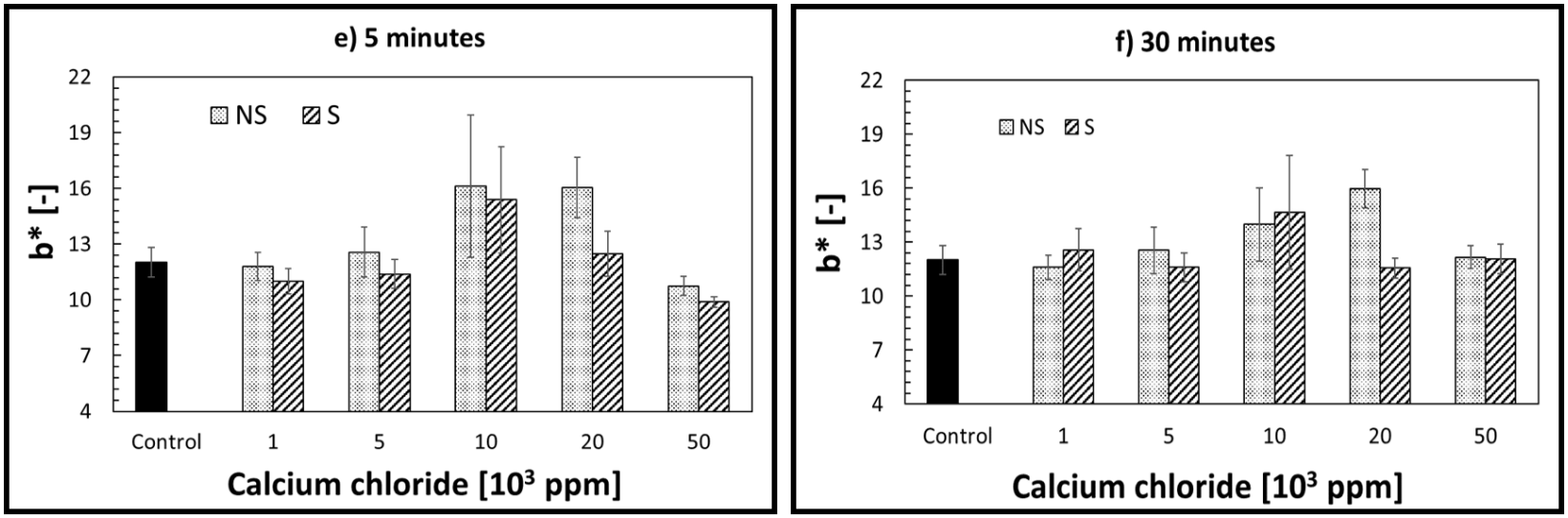
L* [-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	6.6499	1.9546	0.1642	S/NS	1	1.1188	0.3811	0.5380
Conc	4	1543.6504	113.4317	<.0001*	Conc	4	915.4495	77.9554	<.0001*
S/NS*Conc	4	29.2682	2.1507	0.0774	S/NS*Conc	4	33.7079	2.8704	0.0251*

Figure 5. 17. Mean values and two-way ANOVA results for the color parameter "L*" at time duration of 5 minutes (a) and 30 minutes (b).



a* [-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	0.4533	7.2882	0.0078*	S/NS	1	1.01491	29.9462	<.0001*
Conc	4	19.5265	78.4713	<.0001*	Conc	4	3.7820	27.8984	<.0001*
S/NS*Conc	4	1.4449	5.8068	0.0002*	S/NS*Conc	4	7.4864	55.2240	<.0001*

Figure 5. 18. Mean values and two-way ANOVA results for the color parameter "a*" at time duration of 5 minutes (c) and 30 minutes (d).



b* [-]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	78.3449	24.7996	<.0001*	S/NS	1	22.8483	10.7874	0.0013*
Conc	4	613.4473	48.5458	<.0001*	Conc	4	145.7246	17.2003	<.0001*
S/NS*Conc	4	44.9502	3.5572	0.0084*	S/NS*Conc	4	146.5603	17.2989	<.0001*

Figure 5. 19. Mean values and two-way ANOVA results for the color parameter "b*" at time duration of 5 minutes (e) and 30 minutes (f).

5.5.3 Densities – bulk (apparent) and solid

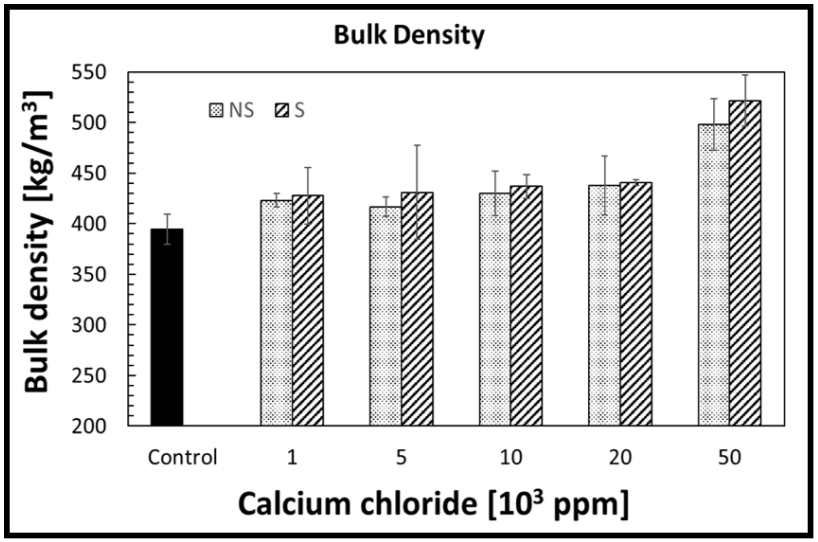
There was a statistically significant ($p < 0.05$) effect of the main factor concentration, indicating that the physical properties solid density and the bulk density responses in the samples change with concentration.

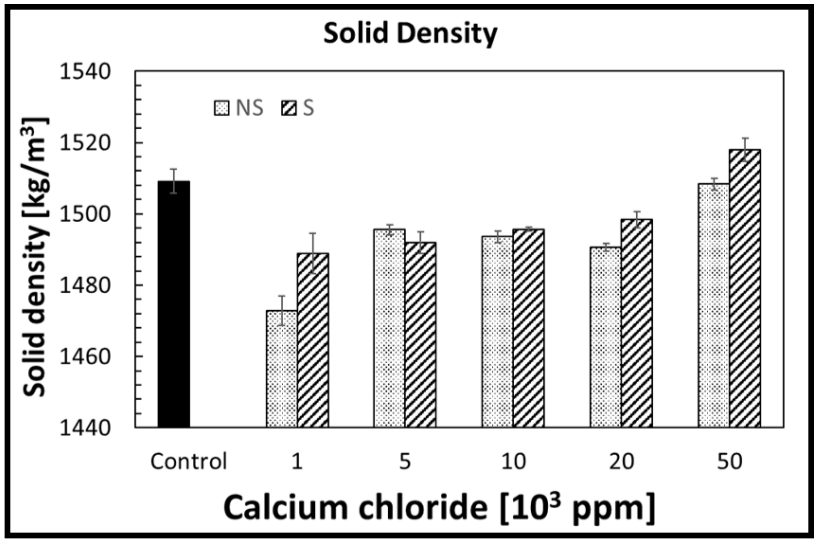
There was a statistically significant ($p < 0.05$) effect of the main factor (S/NS), indicating that the solid density responses in the samples change with S/NS. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at both times, 5 and 30 minutes.

This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists for the solid density factor, but no evidence was found for the bulk density factor (Figure 5.20).

5.5.4 Porosity

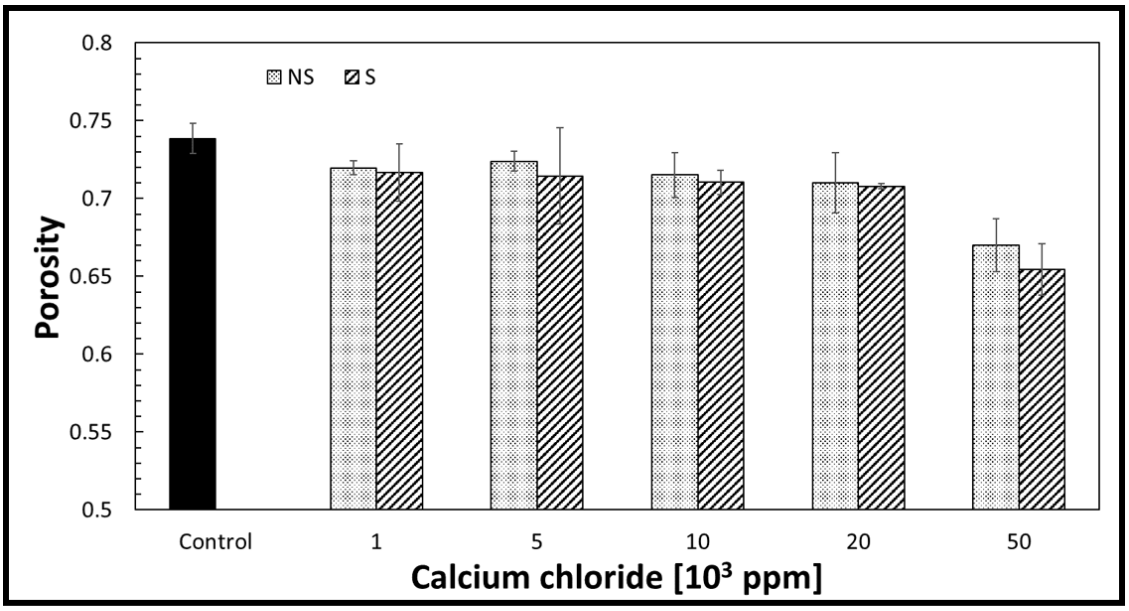
There was a statistically significant effect of the main factor concentration, indicating that the porosity responses in the samples change with concentration. This test also showed no evidence that a statistically significance ($p > 0.05$) for the interaction of both main factors exists (Figure 5.21).





Bulk Density					Solid Density				
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/N	1	31.592	0.0542	0.8183	S/N	1	386.5623	47.2411	<.0001*
Conc	4	31240.743	13.3921	<.0001*	Conc	4	3189.5196	97.4464	<.0001*
S/N*Conc	4	434.282	0.1862	0.9429	S/N*Conc	4	338.3157	10.3362	0.0001*

Figure 5. 20. Mean values and two-way ANOVA results for the bulk and solid densities.



Factors	DF	Sum of Squares	F Ratio	Prob > F
S/N	1	0.00001	0.0542	0.8183
Conc	4	0.0137	13.3921	<.0001*
S/N*Conc	4	0.0002	0.1862	0.9429

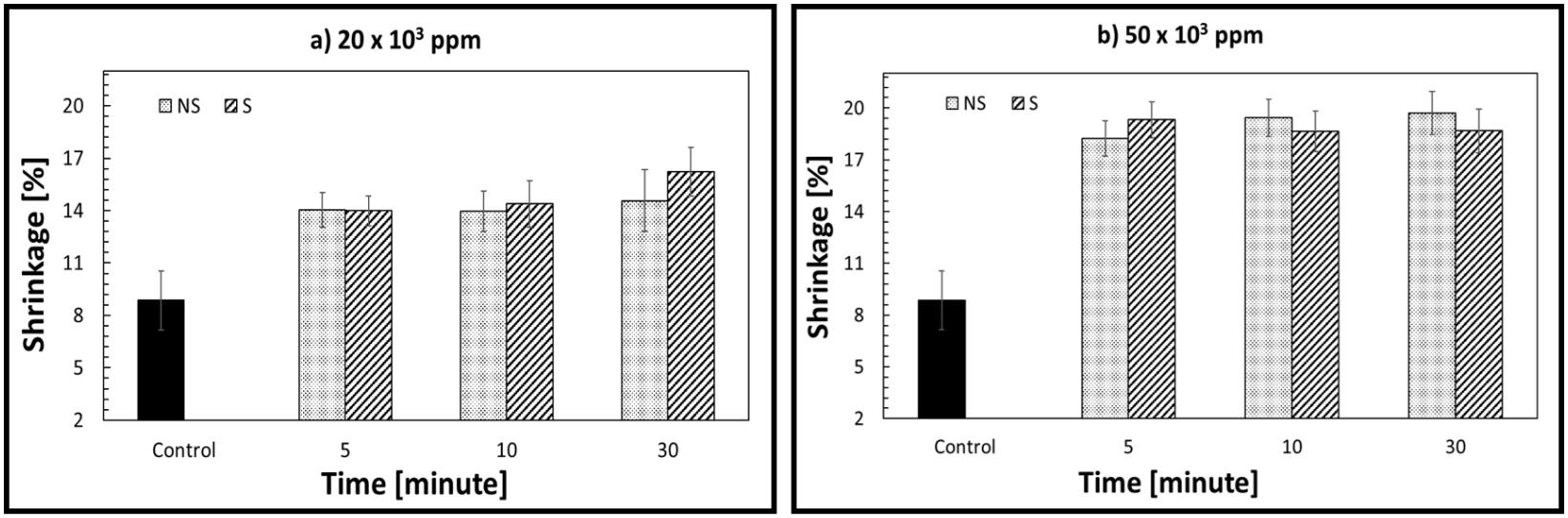
Figure 5. 21. Mean values and two-way ANOVA results for the parameter porosity.

5.5.5 Shrinkage

At the 20 x 10^3 ppm treatment, there was a statistically significant ($p < 0.05$) effect of both main factors (S/NS, time), indicating that the shrinkage responses in the population differs as a function of time and sonication/non-sonication. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at both concentrations (Figure 5.22).

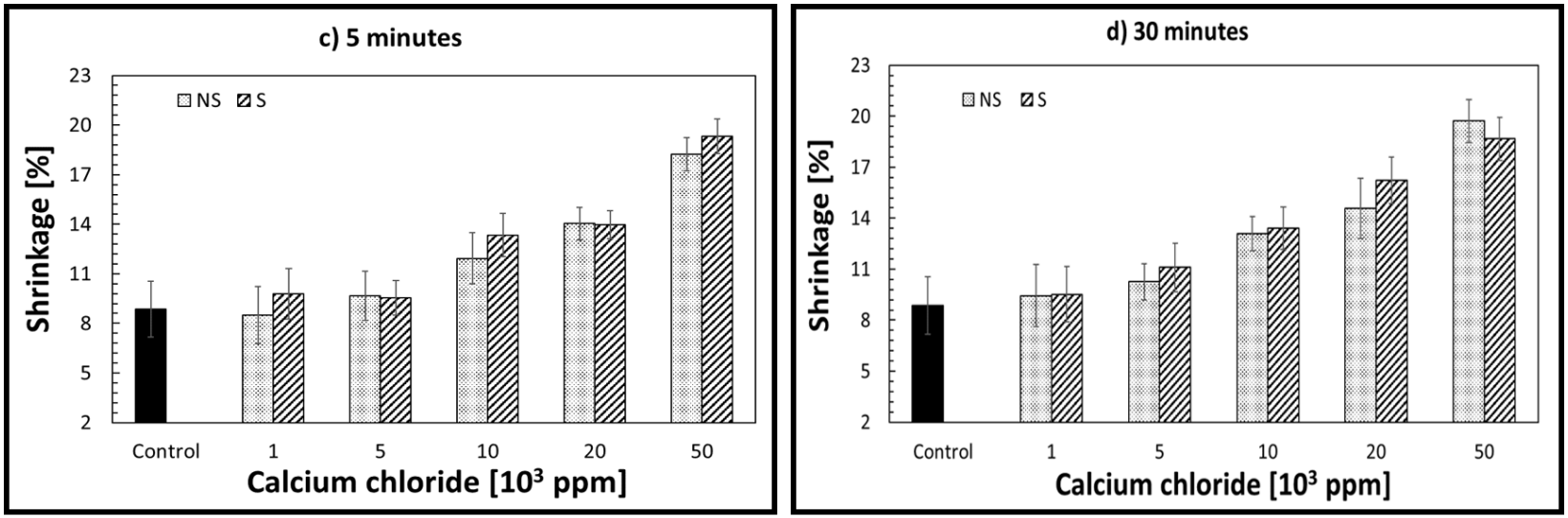
At both treatment times, 5 and 30 minutes, there was a statistically significant ($p < 0.05$) effect of the main factor (concentration), indicating that the shrinkage responses in the population differs as a function of concentration.

There was a statistically significant effect ($p < 0.05$) of the main factor (S/NS), indicating that the shrinkage responses in the population change with S/NS only at the 5 minutes treatment. This test also showed evidence that a statistically significance ($p < 0.05$) for the interaction of both main factors exists at both times, 5 and 30 minutes (Figure 5.23).



Shrinkage [%]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	10.7095	6.5076	0.0125*	S/SN	1	1.3862	1.0592	0.3062
Time	2	35.3756	10.7479	<.0001*	Time	2	2.8508	1.0891	0.3409
S/NS*Time	2	12.0897	3.6731	0.0294*	S/SN*Time	2	21.2814	8.1304	0.0006*

Figure 5. 22. Mean values and two-way ANOVA results for the parameter shrinkage at $CaCl_2$ concentrations of 20 x 10^3 ppm (a), and 50 x 10^3 ppm (b).



Shrinkage [%]									
Factors	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**	**Factors**	**DF**	**Sum of Squares**	**F Ratio**	**Prob > F**
S/NS	1	13.1479	8.2737	0.0046*	S/NS	1	0.0436	0.0217	0.8831
Conc	4	1941.1588	305.3823	<.0001*	Conc	4	1886.7714	234.6752	<.0001*
S/NS*Conc	4	23.0984	3.6338	0.0074*	S/NS*Conc	4	30.9685	3.8518	0.0052*

Figure 5. 23. Mean values and two-way ANOVA results for the color parameter shrinkage at time duration of 5 minutes (c) and 30 minutes (d).

5.6. Sensory evaluation

The one-way ANOVA test was used to verify statistical significance ($p < 0.05$) among the treatments for sensory quality attributes evaluated by 32 panelists.

No statistical significance ($p > 0.05$) was found for any of the three treatments (control, S, and NS) for the sensory quality attributes "Appearance", "Color", and "Odor". However, the sensory quality attributes "Texture", "Flavor", and "Overall Quality", were statistically significant ($p < 0.05$) among the treatments. The "Sonicated" treatment showed the highest scores for all those three parameters. Statistical results are shown on Table 5.21.

Table 5. 21. One-way ANOVA results for sensory quality attributes of the treatments.

Sample	Appearance	Color	Odor	Texture	Flavor	Overall Quality
Control	7.28 ± 1.35^{a}	6.88 ± 1.68^{a}	6.88 ± 1.66^{a}	6.75 ± 1.67^{a}	6.59 ± 1.50^{a}	6.80 ± 1.37^{a}
NS	7.08 ± 1.69^{a}	6.92 ± 1.37^{a}	6.58 ± 1.72^{a}	7.89 ± 0.88^{b}	7.19 ± 1.35^{b}	7.26 ± 1.20^{b}
S	7.52 ± 1.23^{a}	7.11 ± 1.32^{a}	6.67 ± 1.75^{a}	8.00 ± 1.05^{b}	7.75 ± 1.16^{b}	7.75 ± 1.07^{c}

Mean values ± standard deviations followed by different letters within the same column^{a-c} and different letters within the same row^{x-z} for each response are significantly different ($p < 0.05$) according to ANOVA and Tukey's HSD test.

Panelists scored the samples using a nine-hedonic scale where a score of 1 represented attributes most disliked, and a score of 9 represented attributes most liked. Scores higher or equal to 5 were considered acceptable. A graphical representation of the average scores is shown on Figure 5.24.

Comments given blindly by the panelists attributed the higher scores of the samples treated with $CaCl_2$ to "crispier" texture. Medeiros Vinci et al. (2012) also reported that the addition of $CaCl_2$ clearly provoked a crispier texture, as could be concluded from significantly higher snap and crispness scores for blanched potato treated with $CaCl_2$ (0.05 M) compared to control chips.

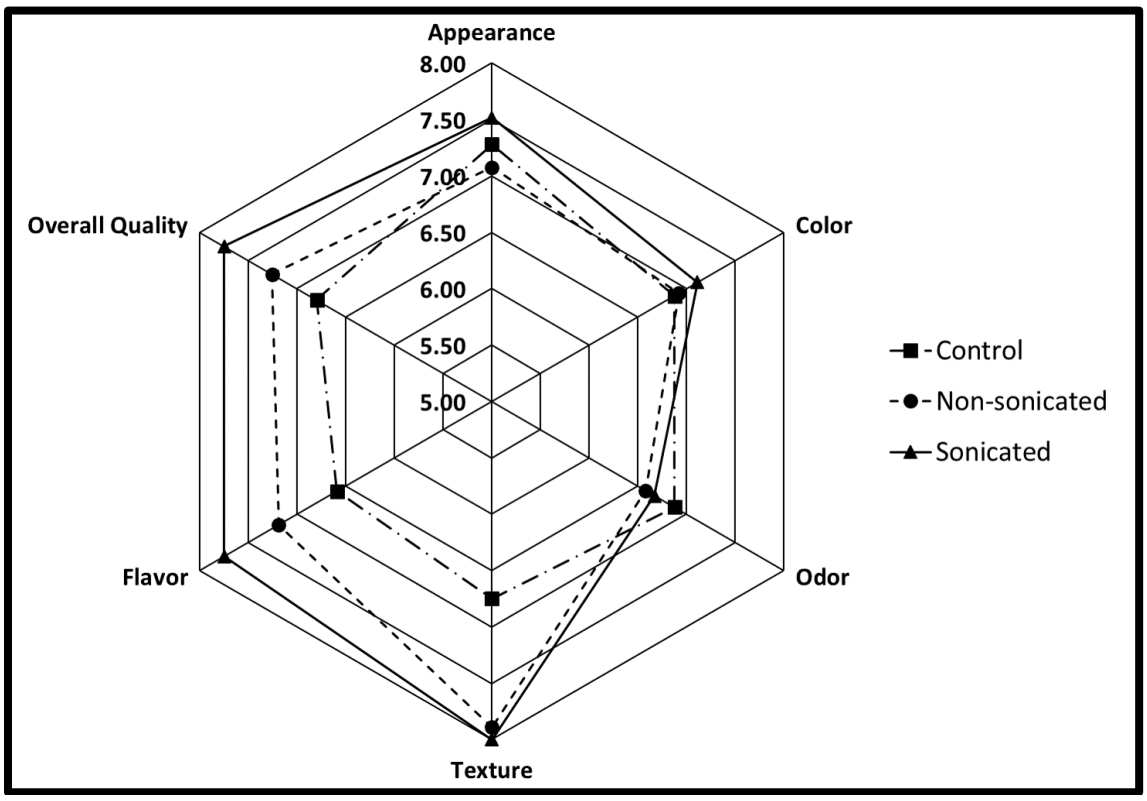


Figure 5. 24. Sensory analysis score-averages for the quality attributes evaluated.

Pictures of the samples taken prior to the sensory evaluation are shown on Figure 5.25. Clearly less blisters (large pockets of air) is presented in the surface of the

sonicated sample. However, it did not affect the appraisal of the panelists for the attribute “Appearance” for the three treatments since they scored statistically ($p < 0.05$) the same values. The smoother surface is similar to chips fried under vacuum, indicative of a more uniform pore distribution (Yagua and Moreira, 2011).

Figure 5. 25. Potato served to the panelists during the sensory evaluation.

5.7. Optical microscopy images

At the highest concentration of calcium chloride, it was difficult to get a sharp image for the cellular structure of the samples, especially for the sonicated ones. It appears that an indirect effect of the sonication might have taken place on the treated samples. These images are merely qualitative, not conclusive. They cannot tell if calcium deposition took place on some specific parts of the potato tissue. Acoustic cavitation resulting from the wave propagation through the material, hence the indirect effect may cause cells to flatten or even rupture (Fernandes et al., 2008, 2009). Perhaps the not so rigid and more rubbery nature of the potato tissue might have been affected by

the ultrasound waves as well. The propagation of the waves will cause zones of rapid alternating pressures through the tissue structure, resulting in zones of compression and expansion, much like a sponge being squeezed and then released. This would cause an exchange of fluids, which is known as the "sponge effect", and it would be difficult to detect it with image techniques since it would take place only during the wave propagation and no permanent damage of the tissue would be left as an evidence that such phenomenon took place.

On a personal consultation with one of the Texas A&M Microscopy Imaging Center staff, a suggestion for the use of the Transmission Electron Microscopy (TEM) associated with Energy Dispersive X-ray Spectrometry microscopy (EDS), the calcium deposition within the potato tissue could be detected. The EDS technique makes the use of the X-ray spectrum emitted by a solid sample bombarded with a focused beam of electrons to obtain a localized elemental analysis, therefore mapping the distribution of that element (any element of atomic number from 4 to 92 can be detected in principle) throughout the solid sample. The scanning electron microscope (SEM), which is closely related to the electron probe, is designed primarily for producing electron images, and it could be used for element mapping, in case calcium deposition was mainly on the surface of the tissue.

Figure 5.26 shows images taken on an optical microscope with a 10X objective magnification. The smaller granular-like clustered structures are the starch granules, the bigger oval like one on images "F" and "G", are water droplets, which were hard to eliminate from the samples in order to get good images. Sonicated (S) - for 30 minutes in

$CaCl_2$, non-sonicated (NS) - for 30 minutes in $CaCl_2$. [1], [5], [10], [20], and [50] denote the concentrations in "x 10^3 ppm of $CaCl_2$". Samples treated for 30 minutes at concentrations equal or higher than 20 x 10^3 ppm of $CaCl_2$ showed barely sharp images as far as the contour of the cells are concerned (H, I, J, K). Visually, differences between sonicated and non-sonicated samples are nearly impossible to be detected. However, these results agree with the "mass transfer" section's results. The loss of turgor of the cellular material treated at those concentrations (20 and 50 x 10^3 ppm of $CaCl_2$) is demonstrated by the lack of sharpness in those images.

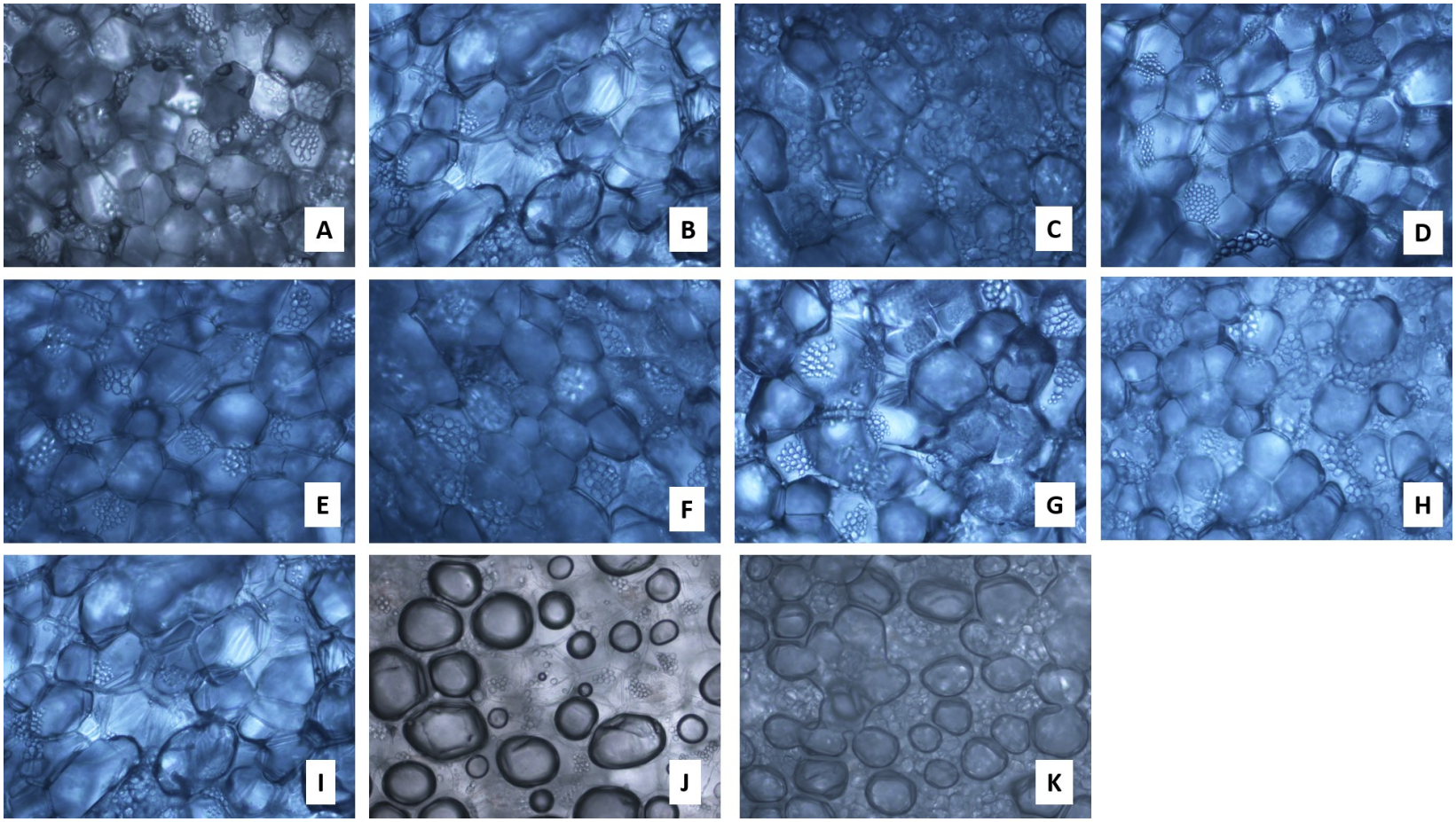


Figure 5. 26. Microscopic images at 10X objective magnification of potato slices for treatments: (A) Control; (B) [1] – NS; (C) [1] – S; (D) [5] – NS; (E) [5] – S; (F) [10] – NS; (G) [10] – S, (H) [20] – NS; (I) [20] – S; (J) [50] – NS; (K) [50] – S.

CHAPTER VI

CONCLUSIONS

This study evaluated the stabilization of potato-tissue's cellular structure to control oil absorption in deep-fat frying of potato chips by using calcium ions (Ca^{+2}). Preliminary studies were carried on using different pre-treatments (soaking, dehydration, enzyme activation, sonication) to assess the changes in structure stabilization prior to frying and to improve Ca^{+2} impregnation in to the cellular material to reduce oil absorption. Parameters generated from the preliminary studies were used to design effective pre-treatments to reduce oil absorption of potato chips during frying. Moreover, parameter quality attributes (texture, color, bulk and solid densities, porosity, shrinkage), sensory evaluation, and microscopic images of the final products and raw material, were also considered in this study.

The main results and conclusions drawn from this study are as follows:

- Soaking pre-treatment of potatoes slices in calcium chloride ($CaCl_2$) solutions and soaking times was effective in reducing the oil absorption in potato chips. The longest time (30 min) at the highest Ca^{+2} concentration (20000 ppm) yielded the lowest ($p < 0.05$) values for oil reduction (26.5%).
- Pre-treatment combinations of dehydration of potatoes slices in ethanolic solution (20% and 70% v/v) with or without Ca^{+2} (10000 ppm) treatment, at different time duration, produced the s lowest ($p < 0.05$) oil reduction (19%)

results for samples pre-treated with EtOH (70% v/v) and $CaCl_2$ (10000 ppm) for 2 minutes.

- Thermally pre-treated samples (50.0ºC/30min) for pectin-methylesterase (PME) activation treated with Ca^{+2} (10000 ppm) had a significant ($p < 0.05$) oil reduction (8.8%).
- The use of ultrasonic waves to enhance mass transfer of Ca^{+2} ions in the soaking and thermal pre-treatments helped decrease oil absorption in potato chips. The soaking pre-treatment ($CaCl_2$ 20000 ppm / sonicated / 30 min) resulted in an oil reduction of 30.2%, and the thermal pre-treatment (Heat + Sonication + $CaCl_2$ 10000 ppm / 60 min) yielded an oil reduction of 14.9%.
- It was estimated through a 4 parameter-logistic model fitting that sonicated samples (30 minutes) started losing mass due to the osmotic pressure of the soaking media at concentrations of 15.7 x 10^3 ppm ($CaCl_2$), and non-sonicated samples at 17.4 x 10^3 ppm ($CaCl_2$). It suggests that sonication can speed up the mass transfer process.
- A Central composite of Response Surface Methodology (RSM) for a three-variables experimental design (*Case 1 – time, concentration, and S/NS*) yielded an optimized pre-treatment of the potato chips in a $CaCl_2$ (17.2 x10^3 ppm) for 15 minutes. The estimated oil content was 0.25 kg oil/kg DM. The preferred treatment was sonication.
- A Central composite of Response Surface Methodology (RSM) for a three-variables experimental design (*Case 2 – time, concentration, and Non-*

sonication) yielded an optimized pre-treatment of the potato chips in a $CaCl_2$ (50.0 $x10^3$ ppm) for 16.5 minutes. The estimated oil content was 0.21 kg oil/kg DM.

- A Central composite of Response Surface Methodology (RSM) for a three-variables experimental design (*Case 3 – time, concentration, and Sonication*) yielded an optimized pre-treatment of the potato chips in a $CaCl_2$ (50.0 $x10^3$ ppm) for 23 minutes. The estimated oil content was 0.16 kg oil/kg DM. This was the longest suggested processed condition with the use of sonication at the highest concentration of $CaCl_2$, however it estimated the lowest oil absorption from all 3 scenarios analyzed.
- The variable "time" for pre-treatment did not show a strong response to the oil content of the final product, however the effect of the variable "concentration" of $CaCl_2$ showed a significant ($p < 0.05$) impact in lowering the oil content of the produced chips.
- Sonicated-treated samples at 20 x 10^3 ppm and 50 x 10^3 ppm of $CaCl_2$ for 30 minutes, showed a decrease in the oil content of the chips by 22% and 43%, respectively, when compared to the control (potatoes not treated with Ca^{+2} and ultrasound).
- From the PQA parameter results, concentration of the $CaCl_2$ solution had more effect on most of the parameters rather than the treatment-time. For the color parameter "L^*", sonicated samples were lighter/whiter than non-sonicated samples. However, the $CaCl_2$ treatment made the samples "darker" as the

concentration of the salt increased. As for texture, hardness of samples from both treatments (sonicated and non-sonicated) increased with $CaCl_2$ concentration increase.

- Bulk and solid density results showed a substantial increase at the highest concentration of $CaCl_2$, with slightly higher values for the sonicated samples.
- Conversely, samples from both treatments (S/NS) had smaller values for porosity at the highest concentration of $CaCl_2$. Significantly higher values for shrinkage were found for both treatments when compared with the control samples.
- No statistical significance ($p > 0.05$) was found for any of the three treatments (Control, Non-sonicated, Sonicated) for the sensory quality attributes of "Appearance", "Color", and "Odor". However, for the sensory quality attributes of "Texture", "Flavor", and "Overall Quality", the results were statistically significant ($p < 0.05$) among the treatments. The "Sonicated" treatment scored the highest values for texture, flavor, and overall quality.

CHAPTER VII

RECOMMENDATIONS

To understand oil uptake in potato chips during deep-fat frying, there is still a need to understand how the chemical make-up of the pores and its structure affect this mechanism.

Recommendations for future research on this area include:

To investigate the use of metal ions (Magnesium, Zinc, Iron, Manganese) and their interaction with the pectic substances in cell wall models and to correlate with cell wall changes under thermal processing and its impact on the cellular structure development.

To study of mechanism of activity of pectin methylesterase, its inhibitors and other wall loosening enzymes to be able to have a controlled cross-linking of the pectic substances to form gels with metal ions *in situ*. This will allow for pore formation control at some extent on real plant-tissue.

Develop reliable methods to characterize surface properties such as roughness, area, surface tension, pore size, and pore size distribution to evaluate the chemical and physical changes induced by the controlled cross-liking of metal ions with the pectic substances throughout the whole processing (raw to fried).

Verify the suitability of scanning electron microscopy (SEM) and the Transmission Electron Microscopy (TEM) associated with Energy Dispersive X-ray Spectrometry microscopy (EDS) to detect and map the distribution of calcium deposition

within the cellular tissue. Study different techniques for substance (mineral and vitamin fortification, antioxidant phenolic extracts for nutraceutical benefits), impregnation in the cellular tissue. Ultrasound has shown an improvement, but there are other techniques like electroporation that uses an electric field to increase permeability of membranes by making it more porous.

Deposition of ultrasound energy, or a reliable measure of its interaction with the material is not well clear. There is need for standardization of methods to obtain consistent results. Fundamental work, looking at the interaction of ultrasound with different materials, characterization of material properties relative to ultrasound such as acoustic impedance, and how this interaction affects the different quality attributes of the material is still required. Once these parameters, properties, and mechanisms are well defined and understood, the optimization of processing parameters can be obtained adequately and will allow the design of processes that will make possible the production of tailor-made food upon the consumers demand. It will bring more versatility to food-processing.

A shelf life study of the potato chips is also recommended since the impact of Ca^{+2} on the lipid oxidative stability was not verified. Moreover, the frying oil should be evaluated for oxidation as well, since Ca^{+2} may leach from the pre-treated potatoes, thus affecting the oil quality.

A study of the economics for production of potato chips using Ca^{+2} ions to reduce oil content is suggested. This technique seems to require lower investment, and manufacturing costs when compared with processes such as vacuum frying. An analysis

of the process feasibility in various production scales is recommended to evaluate its profitability.

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APPENDIX A

Table A-1: Potato slice weight before and after impregnation in calcium chloride at different concentrations for 30 minutes.

Sonicated						
Concentration [ppm]	**BI*[g]**	**Std**	**AI*[g]**	**Std**	**ΔM*[%]**	**Std**
Control	2.16	0.07	2.29	0.08	6.30[a]	0.81
1,000	2.04	0.08	2.18	0.08	6.28[a]	0.88
5,000	2.18	0.06	2.28	0.06	4.55[a]	0.29
10,000	2.09	0.05	2.17	0.05	3.70[a]	0.35
20,000	2.17	0.09	2.17	0.10	-0.05[a]	0.66
50,000	2.18	0.06	2.04	0.05	-6.60[a]	0.41
Non-sonicated						
Concentration [ppm]	**BI [g]**	**Std**	**AI [g]**	**Std**	**ΔM [%]**	**Std**
Control	2.09	0.12	2.24	0.13	6.95[b]	0.28
1,000	1.99	0.13	2.12	0.14	6.85[b]	0.33
5,000	2.27	0.05	2.42	0.05	6.23[b]	0.55
10,000	2.27	0.05	2.42	0.05	6.23[b]	0.29
20,000	2.04	0.10	2.18	0.09	-0.12[b]	0.70
50,000	2.18	0.09	0.10	0.00	0.89[b]	0.00

*BI = before impregnation; AI = after impregnation; DM = percentage change in weight

Table A-2. Hardness values (N) for texture of sonicated (S) and non-sonicated (NS) samples at various $CaCl_2$ concentrations and soaking times.

	Hardness (N)		**Hardness (N)**	
Treatments	$CaCl_2$ - $20x10^3$ ppm		$CaCl_2$ - $50x10^3$ ppm	
[minutes]	NS	S	NS	S
Control	1.28 ± 0.18	1.28 ± 0.18	1.28 ± 0.18	1.28 ± 0.18
5	1.69 ± 0.51	1.68 ± 0.30	1.95 ± 0.76	1.73 ± 0.37
10	1.59 ± 0.17	2.03 ± 0.53	1.44 ± 0.48	1.49 ± 0.42
30	1.39 ± 0.31	1.59 ± 0.34	1.52 ± 0.30	1.51 ± 0.44
	Hardness (N)		**Hardness (N)**	
Treatments	5 minutes		30 minutes	
$CaCl_2$ [10^3 ppm]	NS	S	NS	S
Control	1.28 ± 0.18	1.28 ± 0.18	1.28 ± 0.18	1.28 ± 0.18
1	1.24 ± 0.25	1.25 ± 0.23	1.28 ± 0.32	1.27 ± 0.35
5	1.28 ± 0.39	1.09 ± 0.26	1.24 ± 0.39	1.25 ± 0.28
10	1.50 ± 0.32	1.55 ± 0.33	1.17 ± 0.30	1.60 ± 0.20
20	1.66 ± 0.51	1.69 ± 0.30	1.39 ± 0.31	1.59 ± 0.34
50	1.95 ± 0.76	1.74 ± 0.37	1.52 ± 0.30	1.51 ± 0.44

Mean ± standard deviation of 16 replicates per data set.

Table A-3. Color values (L*, a*, b*) of sonicated (S) and non-sonicated (NS) samples at various $CaCl_2$ concentrations and soaking times.

	Color (L*)		**Color (a*)**		**Color (b*)**	
Treatments	$CaCl_2$ - $20x10^3$ ppm		$CaCl_2$ - $20x10^3$ ppm		$CaCl_2$ - $20x10^3$ ppm	
[minutes]	NS	S	NS	S	NS	S
Control	66.61 ± 0.96	66.61 ± 0.96	-3.20 ± 0.15	-3.20 ± 0.15	12.02 ± 0.80	12.02 ± 0.80
5	61.88 ± 1.25	63.27 ± 1.09	-2.51 ± 0.45	-2.98 ± 0.10	16.07 ± 1.57	12.22 ± 0.60
10	62.55 ± 1.60	64.40 ± 1.08	-3.10 ± 0.31	-3.19 ± 0.12	13.94 ± 0.91	11.33 ± 0.63
30	61.06 ± 0.84	62.28 ± 1.11	-2.48 ± 0.25	-3.27 ± 0.11	15.97 ± 1.07	11.55 ± 0.56
	Color (L*)		**Color (a*)**		**Color (b*)**	
Treatments	$CaCl_2$ - $50x10^3$ ppm		$CaCl_2$ - $50x10^3$ ppm		$CaCl_2$ - $50x10^3$ ppm	
[minutes]	NS	S	NS	NS	S	NS
Control	66.61 ± 0.96	66.61 ± 0.96	-3.20 ± 0.15	-3.20 ± 0.15	12.02 ± 0.80	12.02 ± 0.80
5	57.31 ± 1.46	57.65 ± 1.23	-2.06 ± 0.13	-2.26 ± 0.08	10.74 ± 0.51	9.88 ± 0.30
10	57.53 ± 0.78	58.72 ± 1.26	-1.89 ± 0.09	-2.70 ± 0.05	12.14 ± 0.48	11.71 ± 0.56
30	59.20 ± 1.34	60.14 ± 1.03	-2.17 ± 0.10	-2.76 ± 0.13	12.17 ± 0.63	12.05 ± 0.82
Treatments	**Color (L*)**		**Color (a*)**		**Color (b*)**	
$CaCl_2$	5 minutes		5 minutes		5 minutes	
[10^3 ppm]	NS	S	NS	NS	S	NS
Control	66.61 ± 0.96	66.61 ± 0.96	-3.20 ± 0.15	-3.20 ± 0.15	12.02 ± 0.80	12.02 ± 0.80
1	65.58 ± 2.41	64.93 ± 1.27	-2.70 ± 0.13	-2.64 ± 0.06	11.80 ± 0.76	11.00 ± 0.67
5	66.31 ± 2.69	65.91 ± 1.72	-3.31 ± 0.13	-3.17 ± 0.13	12.56 ± 1.35	11.40 ± 0.78
10	64.08 ± 2.25	65.42 ± 2.20	-2.97 ± 0.47	-3.12 ± 0.31	16.13 ± 3.83	15.38 ± 2.87
20	61.81 ± 1.27	63.24 ± 1.05	-2.52 ± 0.46	-2.94 ± 0.18	16.04 ± 1.62	12.49 ± 1.21
50	57.31 ± 1.46	57.65 ± 1.23	-2.06 ± 0.13	-2.26 ± 0.08	10.74 ± 0.51	9.88 ± 0.30
Treatments	**Color (L*)**		**Color (a*)**		**Color (b*)**	
$CaCl_2$	30 minutes		30 minutes		30 minutes	
[10^3 ppm]	NS	S	NS	NS	S	NS
Control	66.61 ± 0.96	66.61 ± 0.96	-3.20 ± 0.15	-3.20 ± 0.15	12.02 ± 0.80	12.02 ± 0.80
1	66.31 ± 2.00	66.07 ± 1.64	-3.04 ± 0.12	-2.76 ± 0.21	11.59 ± 0.66	12.57 ± 1.18
5	66.20 ± 2.04	64.82 ± 2.49	-2.88 ± 0.13	-2.67 ± 0.23	12.55 ± 1.29	11.60 ± 0.80
10	63.04 ± 2.36	63.35 ± 1.32	-2.81 ± 0.30	-2.74 ± 0.18	13.99 ± 2.03	14.65 ± 3.18
20	61.06 ± 0.84	62.28 ± 1.11	-2.48 ± 0.25	-3.27 ± 0.11	15.97 ± 1.07	11.55 ± 0.56
50	59.20 ± 1.34	60.14 ± 1.03	-2.17 ± 0.10	-2.76 ± 0.13	12.17 ± 0.63	12.05 ± 0.82

Mean ± standard deviation of 16 replicates per data set.

Table A-4. Bulk and Solid densities (kg/m^3), and Porosity (φ) values of sonicated (S) and non-sonicated (NS) samples at various $CaCl_2$ concentrations at 30 minutes of soaking.

Treatment	**Bulk Density (kg/m^3)**		**Solid Density (kg/m^3)**		**Porosity (φ)**	
$CaCl_2$	30 minutes		30 minutes		30 minutes	
[10^3 ppm]	NS	S	NS	NS	S	NS
Control	394.57 ± 14.69	394.57 ± 14.69	1509.13 ± 3.36	1509.13 ± 3.36	0.74 ± 0.01	0.74 ± 0.01
1	423.09 ± 6.86	427.68 ± 27.96	1472.81 ± 4.05	1488.86 ± 5.60	0.72 ± 0.00	0.72 ± 0.02
5	416.56 ± 9.52	430.80 ± 46.48	1495.55 ± 1.39	1491.88 ± 3.06	0.72 ± 0.01	0.71 ± 0.03
10	430.02 ± 21.80	436.96 ± 11.77	1493.59 ± 1.68	1495.70 ± 0.58	0.72 ± 0.01	0.71 ± 0.01
20	437.62 ± 29.15	440.71 ± 2.77	1490.68 ± 1.10	1498.37 ± 2.25	0.74 ± 0.01	0.74 ± 0.01
50	498.05 ± 25.59	521.71 ± 25.03	1508.31 ± 1.72	1518.00 ± 3.24	0.72 ± 0.00	0.72 ± 0.02

Mean ± standard deviation of 3 replicates per data set

Table A-5. Shrinkage values (%) of sonicated (S) and non-sonicated (NS) samples at various $CaCl_2$ concentrations and soaking times.

	Shrinkage (%)		**Shrinkage (%)**	
Treatments	$CaCl_2$ - $20x10^3$ ppm		$CaCl_2$ - $50x10^3$ ppm	
[minutes]	NS	S	NS	S
Control	8.85 ± 1.70	8.85 ± 1.70	8.85 ± 1.70	8.85 ± 1.70
5	14.04 ± 0.98	13.98 ± 0.85	18.23 ± 1.01	19.31 ± 1.04
10	13.96 ± 1.16	14.38 ± 1.33	19.43 ± 1.09	18.66 ± 1.16
30	14.56 ± 1.77	16.23 ± 1.38	19.71 ± 1.26	18.67 ± 1.27
	Shrinkage (%)		**Shrinkage (%)**	
Treatments	5 minutes		30 minutes	
$CaCl_2$ [10^3 ppm]	NS	S	NS	S
Control	8.85 ± 1.70	8.85 ± 1.70	8.85 ± 1.70	8.85 ± 1.70
1	8.51 ± 1.74	9.79 ± 1.54	9.44 ± 1.84	9.52 ± 1.64
5	9.68 ± 1.49	9.54 ± 1.03	10.26 ± 1.08	11.11 ± 1.43
10	11.93 ± 1.54	13.35 ± 1.30	13.09 ± 0.99	13.41 ± 1.26
20	14.04 ± 0.98	13.98 ± 0.85	14.56 ± 1.77	16.23 ± 1.38
50	18.23 ± 1.01	19.31 ± 1.04	19.71 ± 1.26	18.67 ± 1.27

Mean ± standard deviation of 16 replicates per data set