

Physicochemical Transformations in Low-Moisture Dough During Baking

by

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ABSTRACT

PHYSICOCHEMICAL TRANSFORMATIONS IN LOW-MOISTURE DOUGH DURING BAKING

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Transformations in the properties of low-moisture dough products (cookies and crackers) during baking have been studied under idealized conditions in pilot facilities and laboratories. However, little research is published that describes dough development within the context of complex industrial baking processes. A process mapping approach was adopted, in which oven parameters were profiled and matched against changes in dough. In cookies, changes to starch A-granules, including loss of granule birefringence, disruption to granule borders and increased gel viscosity were observed. Development of acrylamide in cookies was seen to trail colour development, suggesting options for mediating acrylamide content. In crackers, the presence of additional water allowed significant changes to starch A-granules to occur, including: swelling similar to the early stages of gelatinization in bread, reduced pasting ability, a drop in enthalpy, and a loss of crystallinity. Emulation of low-moisture dough baking at the benchtop level, based upon internal product temperature data from industrial processes, was found to be limited in its

ability to produce crackers having appropriate leavening and internal structure development.

The determination of isosteric heat of desorption values for cookies and crackers, modeled on industrial processes at temperatures $> 100^{\circ}\text{C}$, gave values of 44.3 and 42.7 kJ/mol, respectively. This data will be useful for establishing energy requirements in industrial baking processes.

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List of Abbreviations

ΔH	Gelatinization enthalpy	[J/g]
ΔH_{vap}	Heat of vapourisation of water	[kJ mol ⁻¹]
AA	Acrylamide	[-]
ANOVA	Analysis of Variance	[-]
a_w	Water activity	[-]
BET	Brunauer-Emmett-Teller	[-]
C_G	Guggenheim constant of GAB model	[-]
CPMG	Carr-Purcell-Meiboom-Gill	[-]
C'	Entropic accommodation factor	[-]
DI	Deionized	[-]
DSC	Differential Scanning Calorimetry	[-]
DVS	Dynamic vapour sorption	[-]
GAB	Guggenheim-Anderson-De Boer	[-]
GDW	Generalized D'Arcy Watt	[-]
h	Apparent heat transfer coefficient	W/(m ² K)
h_c	Convective heat transfer coefficient	W/(m ² K)
H_e	Heat of condensation of pure water	[-]
H_l	Heat of sorption of the multilayer	[-]
H_m	Heat of sorption of the monolayer defined by the BET model	[-]
HMF	Hydroxymethylfurfural	[-]
HMT	Heat-moisture treatment	[-]
h_r	Radiative heat transfer coefficient	W/(m ² K)
HSD	Honestly Significant Difference	[-]
K	Constant of GAB model	[-]
K'	Entropic accommodation factor	[-]
m	Slope of the regression line in the heat transfer coefficient determination method	[-]
NMR	Nuclear Magnetic Resonance	[-]
P	Pressure	[Pa]
Pa	Pascal second	[Pa.s]

Q_{st}	Isosteric heat of sorption	[kJ mol ⁻¹]
q_{st}	Net isosteric heat of sorption	[kJ mol ⁻¹]
R	Ideal gas law constant	8.314510 [J mol ⁻¹ K ⁻¹]
ROI	Region of Interest	[-]
RVA	Rapid Visco Analyzer	[-]
RVU	Rapid Visco Units	[-]
T	Temperature	[K]
T_c	Conclusion temperature	[°C]
T_o	Onset temperature	[°C]
T_p	Peak temperature	[°C]
Std.Dev.	Standard deviation	[-]
X', X''	Constants of GAB model	[-]
X	Moisture content	[kg kg ⁻¹ dry matter]
X_m	Monolayer moisture content	[kg kg ⁻¹ dry matter]

Chapter 1 Introduction

Baking is a multi-billion dollar industry. In Canada, between 2001 and 2010, annual manufacturing revenues from commercial Canadian bakeries rose from \$2.7 billion to \$4.5 billion (Industry Canada, 2013). Within a consumer context, this translates to 4.8% of the average annual household food expenditure (purchased from stores) being spent on bread, unsweetened rolls and buns. A further 2.1% of annual expenditure was spent on cookies and crackers (Statistics Canada, 2013). Given the significant contribution of the baking industry to the economy, and the ubiquity of baked goods in consumers' shopping baskets, it is important that baked products are able to deliver in terms of quality.

Maintenance of product consistency is just one aspect of baked goods quality. This can be elusive when baking ingredients themselves are variable, as in natural products such as wheat flour in which component levels like protein fluctuate (Osella, Robutti, Sanchez, Borrás, & De la Torre, 2008). The impact of such variation was shown in the manufacture of hard pretzels where flour having higher a protein content was shown to produce harder pretzels (Yao & Seetharaman, 2010). Consistency also is affected by the complexity of the baking process itself, a process in which heat and mass transfer transform dough into a finished product having very different attributes by the end of baking. During baking, heat is applied to dough, water is removed, and physicochemical changes take place. The transformations that occur in the product are a result of interactions between the characteristics of the dough and the parameters of the baking

process. The composition of the dough is one way in which baked products are sorted into various categories, such as breads, cookies and crackers (Manley, 2000). The initial moisture content of the dough is one such important parameter, with products such as breads, unsweetened rolls and buns being high moisture products (~70% d.b. dough moisture). Cookies and crackers are low-moisture products with 25 to 40% (d.b.) dough moisture contents. While there have been many studies investigating the physicochemical changes to starch and proteins in high moisture products (Goesaert et al., 2005; Lorenz & Kulp, 1981; Delcour et al., 2010), the physical transformations of these compounds in low-moisture products are less well studied and many authors state that changes to proteins and starches in low-moisture products are negligible (Chevallier, Colonna, Buleon, & Della Valle, 2000; Moiraghi, Vanzetti, Helguera, Leon & Perez, 2011).

Regardless of the moisture content, the changes that take place in baked products occur due to baking. In the simplest of baking processes, such as is typical of domestic ovens, dough is introduced at a single set temperature and baked for a specific time. Industrial baking differs by being a continuous process that takes place in a tunnel oven consisting of multiple zones through which the dough is moved on a conveyor. The zones referred to are discreet areas in which a specific set of process conditions can be applied (Baik, Marcotte, & Castaigne, 2000). For example, all of the burners in the first zone may be at their highest setting and the extractor vents closed, resulting in an area of high temperature and humidity. Multiple oven zones allow operators to effectively begin baking a product in one type of oven and finish it in another, and this approach allows for far finer process control than would be possible in a single continuous oven.

However, as an industrial oven increases in length and number of zones, the kinetics of the transformations occurring in the dough are altered. This makes controlling a process to manufacture products with specific attributes much more complex. Although the physicochemical changes occurring in baked goods are fairly well understood and documented in the literature (for some product categories), this knowledge cannot be easily related to specific product outcomes from industrial ovens. This is because studies on the changes in physicochemical properties that occur during baking are typically conducted using lab or pilot-plant scale ovens intended to replicate baking conditions, rather than in actual industrial ovens (Baik, Sablani, Marcotte, & Castaigne, 1999; Patel, Waniska, & Seetharaman, 2005). While benchtop studies provide an idealised view into the physicochemical transformations in baking, they do not represent the reality of baking as practised in industry. One reason for this is the difficulty of obtaining a complete profile of an industrial baking process that researchers can use as the basis for lab-scale simulations. Acquisition of accurate process parameter data such as temperature and humidity readings from hard to reach areas of an oven is challenging. Also, information on variables such as oven settings and product formulations are commercially sensitive within the industry and thus closely guarded.

This research proposes to better understand the transformations occurring in low-moisture baked products by first assessing actual conditions inside typical industrial ovens and then using this data to interpret product transformations. This approach of mapping the physicochemical transformations of dough against oven parameters throughout the baking process will be referred to as “process mapping”. Process mapping of cookies and crackers are presented in Chapters 3 and 4 of this thesis, while

the physicochemical changes in starch during baking of low-moisture products are discussed in Chapter 5. Energy requirements necessary to remove the water from low-moisture baked products are discussed in Chapter 6. Lastly, Chapter 7 contains overall conclusions and recommendations for future work.

Chapter 2 Literature Review

2.1 Baking – An Overview

Baking is a complex process in which dough is transformed into a final baked product. These transformations include “volume expansion, evaporation of water, formation of a porous structure, denaturation of protein, gelatinization of starch, crust formation and browning reaction” (Sablani, Marcotte, Baik, & Castaigne, 1998). The inputs that make up the baking process can be divided into those that are provided by the oven, and those that come from flour components and ingredient interactions. This literature review provides an overview of current knowledge of each of these types of inputs as they relate to low-moisture baked products baked from low-moisture dough.

In the first section of this literature review, the impact of oven conditions such as heat-energy, air velocity and humidity on baking outcomes are described. In the second section, the composition of baked products is reviewed, and the roles of the major components, i.e., carbohydrates, lipids, proteins and water, are discussed. In the final section, the various transformations that occur throughout the baking process as a consequence of oven parameters acting on the combined dough components are reviewed.

2.2 Ovens: Baking Parameters

Industrial ovens are typically long, linear ovens with many zones that have independent controls. Parameters of each zone that can be controlled include: residence time, temperature, air velocity and humidity, through controls on the damper in the exhaust.

All of these factors influence heat transfer to the product being baked, and as a result, mass transfer within the product. While the time or duration of a baking process is important with respect to final product attributes, it is an extrinsic property and should be considered in association with the other baking parameters.

2.2.1 Temperature & Heat

Setting the temperature for a specific zone modulates the switching off and on of the chosen heat source in the oven zone. This heat source is typically electric or gas, although some ovens end with a microwave section which helps to lower final moisture content and results in a more uniform moisture distribution (Chavan & Chavan, 2010). However, it is a more complicated combination of factors, such as burner placement and the materials from which the oven is constructed, that determine the quantity of each type of heat that is delivered to the product being baked. The rate at which that heat is being delivered is also important. This rate of heat transfer per unit area (measured in watts, or joules per second) is known as heat flux (W/m^2) (Zareifard, Marcotte, & Dostie, 2006). In industrial ovens, the modes of heat transfer to the baked product include: conduction, convection, and radiation (Figure 2.1).

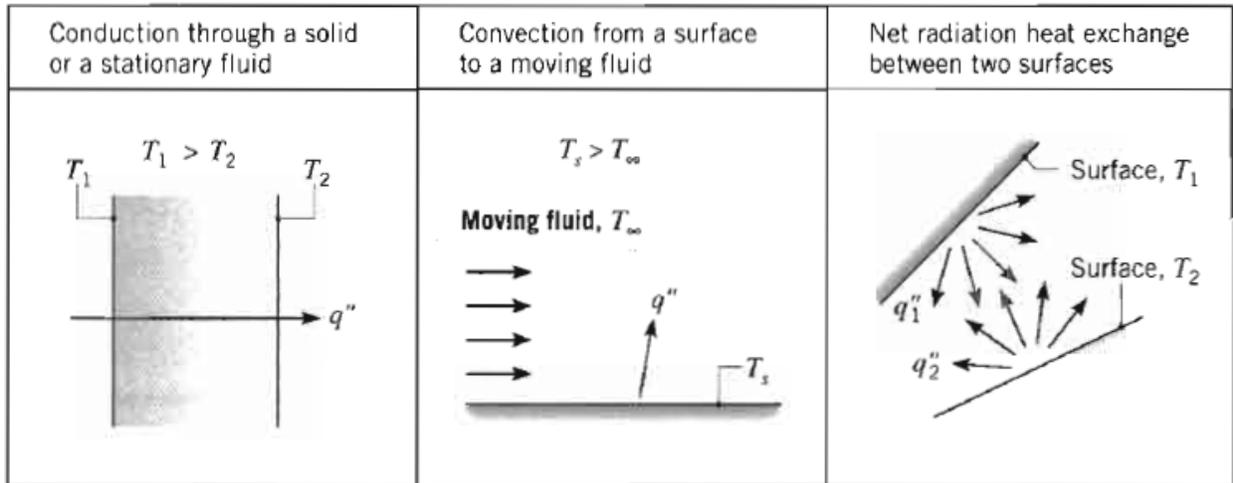


Figure 2.1 Conduction, convection and radiation heat transfer modes - adapted from Incropera, DeWitt, Bergman, & Lavine, (2006)

In conduction mode, heat transfer occurs across a solid or a stationary fluid in which there is a temperature gradient. As shown in Figure 2.1, heat is conducted across the medium in direction q'' , from an area of higher temperature T_1 , to an area with a lower temperature, T_2 . During baking in an industrial oven, the mediums for heat conduction are the oven band and the product itself. Heat transfer from the oven band to the bottom surface of the baked product it is in contact with, and heat transfer from the surface to the interior of the dough piece, are examples of conduction.

In convection mode, heat transfer occurs between a surface and a moving fluid that are at different temperatures. During baking, convection occurs when heat is transferred from the heated air to the surface of the product being baked. As shown in Figure 2.1, convective heat transfer occurs from the higher temperature surface T_1 , to the moving fluid in direction q'' .

In radiation mode, heat transfer occurs by emission of electromagnetic waves when two surfaces are at different temperatures. As shown in Figure 2.1, without any medium

between them, there is a net transfer in directions q_1'' and q_2'' of heat between the two surfaces at different temperatures T_1 and T_2 . Examples of heat transfer by radiation during baking are: heat transfer from a heating element or flame to the surface of the dough piece, and heat reflected from oven walls to the dough piece.

The proportion of each type of heat that the product is exposed to has a major influence on the physicochemical properties and attributes of the final baked product. When only radiant heat is provided, evaporation of water out of dough is slowed as there is little convective air movement to disrupt the stagnant moisture boundary layer. The associated lack of evaporative cooling also leads to higher surface temperatures and thus a greater degree of browning from radiative heating (Standing, 1974). Conversely, when only convective heat is applied, rapid expansion is followed by structural collapse as leavening takes place more rapidly than the development of a self-supporting matrix of starch and protein (Manley, 2000). Baking without radiative heat may also result in insufficient browning. Therefore, an optimal balance of radiative and convective heat during baking is necessary to ensure that the desired characteristics are achieved in baked products (Zareifard, Boissonneault, & Marcotte, 2009).

2.2.2 Air Velocity

Air velocity in an oven affects transfer of radiative and convective heat. This is due to an increased air velocity leading to an increase in the apparent heat transfer coefficient, h ($W/m^2 K$), as shown in equation 1,

$$h = h_r + h_c \quad [1]$$

where h_r is the radiative heat transfer coefficient, and h_c is the convective heat transfer coefficient (Sato, Matsumura, & Shibukawa, 1987). Movement of product during baking, as is the case with tunnel ovens, has the effect of moving air relative to the product. This natural air velocity is determined by oven band speed. Ovens also may be deliberately designed to capitalise on convective air currents resulting from heat sources, and this also increases air velocity around the product. Altering air velocity during baking changes the balance of convective and radiative heat, with increased air velocity being tied to changes such as increased product weight loss (by greater water removal) and decreased browning. To clearly see the effect of air velocity on apparent heat transfer coefficient, it is useful to examine jet impingement ovens, which are an extreme case of high air velocity being used in a baking process (Sarkar, Nitin, Karwe, & Singh, 2004). A study by Nitin & Karwe (2004) used model aluminum cookies placed in an impingement oven with jet velocities of 10, 20, 30 and 40 m/s being directed to the “cookies” upper surface. Increasing velocities resulted in increasing heat transfer coefficient. The use of aluminum cookies as a substitute for cookie dough in modelling of oven heat transfer was justified, as surface heat transfer coefficients were found to be the same, i.e. independent of the thermo-physical properties of the objects. This property is useful as it allows engineers to build an idealized model of heat transfer in an oven without confounding inputs from variable food materials. Actual surface temperature values for food material was found to be significantly lower than those of aluminum in this experiment, and this was anticipated as the thermo-physical properties of each material were very different (food having lower density and thermal conductivity, and higher heat capacity). Air velocities encountered in typical industrial baking

processes are much lower than in impingement ovens, with values up to approximately 1.5 m/s being typical. This can still make a significant contribution to heat transfer in baking, as in a 200°C process, air velocities of 0.5, 1.0 and 1.5 m/s result in heat transfer coefficients of approximately 9, 16 and 21 W/m²K, respectively (Sato et al., 1987).

2.2.3 Humidity

The moisture held in the air inside a tunnel oven during baking is present as a result of water being removed from the product. An additional smaller proportion of humidity is also attributable to gas-combustion, when gas-fired ovens are being used (Baik et al., 2000). The measurable absolute humidity in an oven will be influenced largely by venting of moist air throughout the process. While warmer air has the ability to hold more water than cooler air, it is still important that humidity is controlled around the product by exhausting moist air during the baking process through exhaust vents. This is essential because variation in humidity is responsible for quality defects in baked products (Baik et al., 2000). Conversely, the ability to maintain appropriate humidity during baking is linked to improved quality characteristics in cookies. Specifically, cookie spread factor (width/thickness ratio as per AACCI Method 10-50.05) and colour L* value (CIE L*a*B* colour space) increase with increasing humidity, as per Table 2.1.

Table 2.1 Effect of absolute humidity on cookie quality attributes. Adapted from, Xue, Lefort, & Walker, (2004)

Absolute Humidity (g H ₂ O/kg dry air) (Mean)	Colour (L* value)	Spread ratio (width/thickness)
14.2 ± 1.48	63.4 ¹	7.6 ± 0.1
18.8 ± 3.19	64.9	7.7 ± 0.2
28.6 ± 3.7	65.2	7.9 ± 0.1

¹ 0 = black, 100 = white

Oven humidity also is recognized as an important factor influencing the quality of bread during baking, and bread ovens incorporate steam injection in order to better produce loaves with desirable characteristics. When less steam is injected, bread crust forms rapidly, leading to the buildup of a high internal pressure in the loaf and subsequent tearing of the crust at the base of the loaf. When greater amounts of steam are injected, moisture condenses on the surface of the loaf and acts as a plasticizer allowing the crust to expand without tearing (Le-Bail et al., 2011). The same study also showed that the kinetics of heating during baking are influenced by the amount of steam used: at low levels of steam, moisture did not condense on loaves during baking, whereas at higher levels of steam, condensation occurred. Heating rate is greater at low steam levels and lower at high steam levels, as heating of the loaves under high steam conditions requires heat energy to be used to evaporate the condensed moisture.

The baking of cookies in industrial tunnel ovens also requires high humidity early in baking. In this case greater humidity is achieved by not venting the moist air generated

from the initial drying of the dough. As in bread baking, some of the moisture condenses on the cookie dough pieces, allowing a greater degree of spreading and also more surface cracking (Manley, 2000).

As outlined in this section, each of these oven parameters can be altered to affect baking outcomes, and this has promoted the idea of process optimization as a means to achieving the most desirable attributes in a product. In order to allow manipulation and control of oven parameters in these studies, baking is generally carried out on a benchtop or pilot-scale oven. Such ovens have been used for a number of baked products. A BRI Australia Limited (formerly the Bread Research Institute) oven simulator (APV Baker Pty) was used to simulate a four-zone industrial bread oven in which temperature, air velocity and baking time were manipulated, allowing an optimal temperature to be determined for baking in each zone such that loaves with the lowest possible weight loss could be baked (Therdthai, Zhou, & Adamczak, 2002). Almond paste cookies also have been made in a pilot-scale oven where baking time and temperature were manipulated in step with dough formulation according to a response surface methodology (Farris & Piergiovanni, 2009). While this is useful on a small scale, the difficulty of applying such fine controls to specific areas of an industrial oven, as well as expense, make the use of large-scale industrial baking processes impractical for such research. At the same time, the scale of industrial ovens, their use of multiple zones, and the difficulties associated with knowing the values of specific parameters on a moment-to-moment basis make their accurate replication at a lab scale an elusive goal. Therefore, one goal of this research was to better understand the effects that the baking parameters inside actual industrial tunnel ovens have on product attributes.

2.3 Composition of Baked Products

In order to better understand the baking of low-moisture products, it is necessary to understand the composition of the dough used in these processes. This section provides an overview of the functional roles of the key components of cookies and crackers. Water, a key component, is discussed in the context of the other components. In addition, the importance of water content to the attributes of low-moisture baked products, and the energy requirements to remove water, also are discussed.

2.3.1 Carbohydrates

Starch

The primary ingredient in cookies and crackers is wheat flour, and the main component of that flour (>60%) is starch (Csiszár et al., 2010). While the role of starch in high moisture dough products, like bread, that contains approximately 70% moisture (d.b.) is fairly well understood, there is a tendency to dismiss starch in low-moisture dough products, like cookies, or crackers, as having no functional role beyond that of filler. In bread, starch swells as it takes on water and gelatinizes during baking. Amylose leaches from granules, and upon cooling forms double helices and a continuous crystalline network. In this way, starch contributes to the structure of bread crumb (Delcour et al., 2010). This contrasts with the role of starch in low-moisture dough products. In these systems, the starch granules remain unchanged and simply become “embedded in a matrix of aggregated protein, lipids and sugars” (Chevallier, Colonna, Della Valle, & Lourdin, 2000). However, changes to starch during thermal processing of

a low-moisture dough has been shown in the case of low pressure cooking (Marti, Pagani, & Seetharaman, 2011). In that study, pasta dough (40% d.b.) made from rice flour exhibited a loss of order consistent with thermal treatment when observed by X-ray diffraction. Research on starch transformations in cookie baking, however, showed little change to the starch granules, beyond a partial loss of birefringence and some limited swelling (Chevallier, Colonna, Buleon, et al., 2000). In contrast, crackers contain a greater proportion of water than cookies, but considerably less water than breads. Therefore, it is hypothesized that starch transformation in crackers may be intermediate to these products in nature. That is, the initial stages of gelatinization, such as granule swelling, may occur alongside limited leaching of amylose.

Sugars

Carbohydrates in the form of sugars account for approximately 5.8% by weight of a snack cracker formulation and from 17.6-31.2% by weight of cookie formulation, with sucrose being one of the most important sugars in industrially-produced products (Kweon, Slade, & Levine, 2011a; Pareyt, Talhaoui, Kerckhofs, Brijs, Goesaert, Wevers & Delcour, 2009). Incorporation of sugars in these products is important for many reasons beyond just sweetness. For example, sugars contribute to colour and flavour development via caramelization (Kroh, 1994) and also via the Maillard reaction (Becalski, Lau, Lewis, Seaman, Hayward, Sahagian, Ramesh & LeClerc, 2004). Sucrose contributes to the characteristic hardness and snap of cookies due to its melting during baking and subsequent transition to a glassy state upon cooling (Chevallier, Colonna, Buleon, et al., 2000). The crystal size of sucrose added to cookies

also has an effect on quality, with smaller crystals leading to greater surface cracking in sugar-snap cookies, and greater spread and associated lower height in wire-cut cookies. This is because larger sucrose crystals have a longer dissolution time than smaller crystals, allowing for a greater degree of gluten development and starch gelatinization (Kweon, Slade, Levine, Martin, & Souza, 2009).

2.3.2 Lipids

Lipids are added to baked products for a variety of reasons. In breads, where lipid is only approximately 1.5% by weight of the formulation, it is added to improve machinability, specifically slicing of the finished product (Mondal & Datta, 2008). The lipid content of cookies is much greater at 10-19% by weight where it is added primarily as a shortening agent, i.e. it inhibits gluten development during forming of the dough. Cookie dough with a lower lipid content has been shown to produce harder cookies, as determined using a three-point bend test (Mamat, Abu, & Hill, 2010). The lipid content of a cookie dough is also known to contribute to dough plasticity, allowing the dough to flow under the influence of gravity when heat is applied (Chevallier, Colonna, Buleon, et al., 2000). Lipid addition to low-moisture baked products such as cookies also is important due to the ability of the lipid to incorporate air, with air cell size shown to increase with increasing lipid addition in sugar-snap cookies (Pareyt et al., 2009).

2.3.3 Proteins

The wheat flour that is used contributes to the protein content of baked goods. For crackers, a higher protein flour of 9-10% is typical, whereas for cookies 7-8% protein

content is more usual (Osella et al., 2008). In other baked products, like bread, the protein content is vitally important to the development of a gluten matrix, imparting the dough with a degree of extensibility that allows the development of the characteristic leavened structure. The lower relative proportion of flour, based on dry ingredient weight, and thus protein, in cookies and crackers versus breads, results in very different structural properties. In cookies, which have the highest amounts of both fat and sugar in comparison to protein, development of gluten is very limited. This is because protein competes for any available free water with the other ingredients (Moiraghi et al., 2011). Protein entanglement and cross-linking of gluten during baking of cookies is also delayed and inhibited as sucrose concentration increases (Pareyt, Brijs, & Delcour, 2009). If a protein network is formed in cookies, it alters cookie structure by reducing spread. In crackers the higher protein content of the flour used compared to cookies and the lower levels of sugar in the cracker dough allows protein hydration and promotes gluten development during mixing and sheeting (Kweon et al., 2011a). When protein levels are higher in crackers, there can be excessive shrinkage of the dough piece during baking, and an associated increase in cracker toughness (Osella et al., 2008).

2.3.4 Water

The amount of water initially present in dough, rather than the final moisture content of the product, is key to the classification of a low-moisture baked product, and this distinction separates cookies and crackers from twice-baked products such as croutons even though they also have a final moisture content of approximately 3-5% (d.b.). This

is because the initial moisture content of dough influences component interactions and thus final product attributes by facilitating transformations within products during baking. For example, bread dough has a higher moisture content ($\approx 70\%$ d.b.) compared to cracker dough ($<40\%$ d.b.), and the greater availability of water in bread dough facilitates gelatinization of starch, and mobility of proteins during baking (Mondal & Datta, 2008).

One of the main functions of the baking process is to remove water from dough. However, in food products water is held in three ways which influence its ease of removal. These are as a monolayer, via polymolecular sorption and as capillary condensation (Figure 2.2).

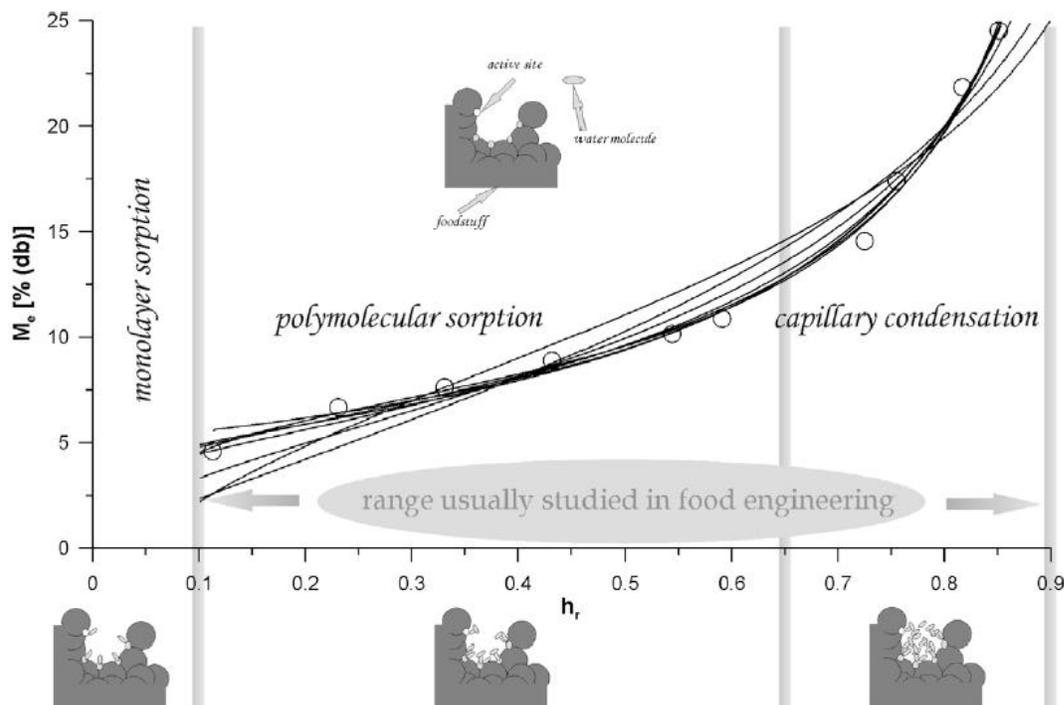


Figure 2.2 Schematic of the three stages of water sorption mechanism on chickpeas at 293 K. Adapted from Furmaniak, Terzyk, Gołembiewski, Gauden, & Czepirski, (2009).

Each of these types of water binding is related to a range of water activity values.

Sorption isotherms, such as that shown in Figure 2.2, are a useful way of representing the change in moisture content of a food versus its water activity (McLaughlin & Magee, 1998). Because of differences between foods, sorption (and desorption) isotherms are specific to a food product and must be determined experimentally. This is typically done using the dynamic vapour sorption (DVS) method in which the humidity around the food is held in a steady state until equilibrium is reached. To establish points on the isotherms, the food is weighed and the equilibrium mass value is used to calculate the isotherm value for that point. The humidity is then adjusted and the process repeated until sufficient points to plot the isotherm have been collected. Because of the need to reach equilibrium at each step, it can take several weeks to collect isotherm data.

Although establishing isotherms is time consuming, it is carried out for many foods because this knowledge is useful for designing, modeling, and optimizing effective dehydration processes (McLaughlin & Magee, 1998; Furmaniak et al., 2009). However, isotherms also change with changing temperature, which makes measurement and prediction of isotherms at the temperatures encountered during baking difficult. One solution is to collect a smaller number of isotherm data points and then to use a model to fit the isotherm. There are a number of models available for this purpose including those of: Brunauer-Emmett-Teller (BET), Chung and Pfoest, D'Arcy and Watt (GDW), Guggenheim-Anderson-De Boer (GAB), Halsey, Henderson, and Lewicki (Oswin equation) (Clemente, Bon, Benedito, & Mulet, 2009; Furmaniak et al., 2009; Moraes, Rosa, & Pinto, 2008). The GAB model has been shown to be a good fit for many foods, e.g. apples, garlic, and previously frozen raw pork, particularly when data is fitted over a

wide range of water activities and up to a water activity of 0.9 (Prothon & Ahrn, 2004; Clemente et al., 2009). A study of a number of food products, including: marjoram, dill, granulated garlic, semolina, skim milk powder and ground coffee, at low humidity levels found that the GDW model provided a better fit than the GAB model, and this was suggested to be a result of the GAB model being a simplified form of the GDW model (Furmaniak et al., 2009). In baked goods (gingerbread cookies with a moisture content of 8% d.b.) the GAB model was found to fit data obtained at 20, 25 and 30°C better than the BET model (Cervenka, Rezkova, & Kralovsky, 2008). Establishment of a good fit when modeling sorption and desorption isotherms is important to the accurate determination of isosteric heats of sorption and desorption for a product. This is because the Clausius-Clapeyron equation is applied to the modeled isotherms at different temperatures in order to calculate isosteric heats which are “differential molar quantities derived from the temperature dependence of the isotherms” (Wang & Brennan, 1991). By finding the isosteric heat of desorption for a product, it is then possible to calculate the amount of energy that is required to remove a known amount of water from it during baking (Moraes et al., 2008). Having a theoretical minimum amount of energy as a target for a baking process is important for modeling or designing a new process. Isosteric heat of desorption is related to the amount of energy needed to break the intermolecular attractive forces between the water molecules and the sorption sites in a food that are illustrated in Figure 2.2 (Moraes et al., 2008). The lower the moisture content of a food, the greater the isosteric heat of desorption. This is due to water sorption at low-moisture levels occurring only at the high energy active sites, and as moisture content increases sorption occurs at increasingly less active sites

that require less energy for desorption. Isothermic heat decreases with increasing moisture content until it approaches the heat of vaporization of pure water (Wang & Brennan, 1991). While isothermic heat values have been determined for some low-moisture baked goods, this has been for adsorption of water at characteristic storage temperatures in order to provide information for shelf life predictions and moisture gain relating to product acceptability (Palou, Lopez-Malo, & Argai, 1997; Sampaio, Marcos, Moraes, & Perez, 2009). There is still work to be done determining isothermic heat of desorption values for low-moisture baked goods, particularly at the elevated temperatures found during baking.

The components of low-moisture baked products have various functional roles in baking. The contribution of these components to product structure and function does not occur in isolation, as baking promotes interactions between the components. A further aim of this research was to examine interactions such as those between starch and water in low-moisture products (crackers) versus very-low-moisture products (cookies).

2.4 Transformations in Low-Moisture Products During Baking

Baking involves transforming dough into a finished product by removing moisture and setting product structure. The initial moisture content of dough is important to the component interactions and product attributes of baked goods and impacts the transformation of dough into products with specific desired attributes. Low-moisture baked products are extremely diverse in their composition, but largely can be grouped as cookies or crackers. Cookies are distinguished by being short dough products with very low initial dough moisture contents, often less than 20% (d.b.). In cookies, plasticity

is conferred by sugar and fat, and the cohesiveness of such short dough has been determined to be unrelated to any action of proteins such as gluten (Chevallier, Colonna, Buleon, et al., 2000). Crackers, on the other hand, contain a greater proportion of water, less sugar and less fat. Flour used in cracker production also is typically higher in protein (9-10%) than that used for cookies (7-8%) (Osella et al., 2008). This greater amount of protein results in the development of a gluten-based matrix, while the additional water may enable gelatinization of a proportion of the starch within crackers during baking. Although cookies and crackers are relatively simple mixtures of flour, water, fats, sugars, salt and leavening agents, baking promotes complex interactions between these components, leading to many changes in their physical and chemical properties. These broadly include changes in product dimensions, modification of textural properties, development of colour, and alteration of chemical composition.

Despite the parameters of their baking processes being highly complex, industrial bakeries continue to produce baked goods within tight quality control parameters, while being controlled by operators who have little direct knowledge of oven conditions. The following section describes the transformations that occur in dough as it is baked. The physicochemical transformations that occur are a result of the oven parameters described in section 2.2 acting on the dough components described in section 2.3.

2.4.1 Change in Product Dimensions and Modification of Texture

The influence of heat and the action of leavening agents are vital contributors to the changes in dimensions that occur when cookies and crackers are baked. Heat

conducted from the oven band, transferred via convection of the air inside the oven, and radiated heat from the oven walls serves to warm the dough and melt the fat component. The dough becomes more plastic and flows under the influence of gravity, leading to an initial spreading (Hoseney & Rogers, 1994). While this is true in cookies such as AACC wire-cut cookies (Method 10-53.01), which are approximately 19% fat by weight, the lower fat content of crackers such as snack crackers, with only 8% fat, precludes this type of spread. Heat also has the effect of warming water in dough, which increases water vapour pressure. This water vapour pressure increase accelerates from around 60°C upwards and contributes to volume increases. Bubbles of air trapped in the dough also increase in volume as the temperature rises, e.g. air raised from 21 to 100°C expands approximately 1.25 times (Matz, 1992).

Cookies and crackers also make use of chemical leavening to change their dimensions. Chemical leaveners react in the presence of heat and moisture to release CO₂. They are typically alkalis, such as sodium bicarbonate or ammonium bicarbonate, and make use of acidic food components or added acids e.g. monocalcium phosphate, to proceed with their reactions. They also will decompose directly to release CO₂ when heated above 80°C (Manley, 2000).

Whether the change in dimensions of dough is a steady linear increase and eventual set, as in crackers, or an expansion followed by a fall-back and set, as in cookies, is largely determined by dough formulation. Cookies are characterized by a rapid initial rise and subsequent collapse. Rising ends as dough viscosity becomes too thick, with protein aggregation occurring from 85°C. A rapid collapse follows as gas production ceases, with the dough matrix not being rigid enough to support itself. Actual set occurs

as sugars go through glass transition on cooling (Chevallier, Della Valle, Colonna, Broyart, & Trystram, 2002).

Warming of dough as baking proceeds leads to an initial softening in texture as fats melt. Leavening creates a more open, lighter structure and decreases density.

However, the final set structures, and thus textural properties, developed in baking of cookies and crackers differ, largely due to their initial compositions. That is, the low initial moisture content of cookies and high sugar content precludes much change occurring to starch, and their crisp texture is obtained by the formation of the sugar's glassy state. In contrast, crackers have an initially greater water content (~35% d.b.) such that starch can contribute to texture along with gluten thermal setting. This, along with localized zones of higher moisture content that occur when water being transported out of the cracker is trapped behind the set cracker surface, allows for limited starch gelatinization.

A short dough is described as an "emulsion of lipids in a concentrated sugar solution" and it is this emulsion which contributes to the physicochemical basis of texture in these systems (Chevallier, Colonna, Buleon, et al., 2000). Following baking, cookie structure becomes a "composite matrix of protein aggregates, lipids and sugars embedding starch granules" (Chevallier, Colonna, Buleon, et al., 2000). The contribution of each constituent to texture has been assessed by submerging dough and cookies in varying solvents and interpreting the resulting structural integrity. The lack of a gluten network in dough and cookies was confirmed. Starch was shown not to contribute to cohesiveness while sugars were shown to provide structure. The structural role of sugars is suggested as being the result of sugars melting during baking and reforming in the glassy state.

Further evidence comes from Chevallier et al., (2002) who described a collapse phase occurring in short dough after the 80-100°C range at which gluten-set occurred.

Conditions were met for protein glass transition ($T_g = 122^\circ\text{C}$ at a water content of 3.2% w.b.) but as the collapse finished in the range of 100-120°C this was considered to contribute to “setting up” but not accounting for development of a set structure. With sugars making up 28% of the dough formulation, and sucrose having an upper T_g of 60°C at 0% moisture, the soft texture during baking and development of crispness on cooling was therefore attributed to sugars moving to the glassy state.

In crackers, a continuous expansion caused by gas from leavening agents occurs, leading to an open and less dense structure. The matrix of starch and protein gels developed is made possible by higher water content and leads to the setting of a self-supporting structure (Manley, 2000). Proteins become sufficiently hydrated to form a gluten network and denature and thermal set above 70°C; the application of heat and the presence of water allow starch gelatinization to occur within the range 52–99°C depending on the influence of other components such as sugars (Mamat et al., 2010).

2.4.2 Development of Colour

The development of colour in baked goods is the result of two simultaneously occurring processes, the Maillard reaction where sugars interact with amino acids, and caramelization which is a direct degradation of sugars (Zanoni, Peri, & Bruno, 1995).

There is also some contribution to colour from the dextrinization of starch, and while burning also changes product colour when temperatures become too high, the result is undesirable (Manley, 2000).

The Maillard reaction begins with the interaction of reducing sugars with amino acids and ultimately results in the creation of melanoidins, which are brown, nitrogenous polymers, and many of the intermediates in this process are very important as contributors to flavour in baked goods (De Man, 1995). Cookies and crackers provide an abundance of starting material for the reaction to proceed through the presence of proteins and sugars. The use of sucrose, a non-reducing sugar, in these products is also not a barrier to the reaction proceeding, as both sucrose and the starch from the flour, are hydrolysed upon heating above 100°C when the pH is slightly acidic, resulting in a constant supply of reducing sugars for the reaction (Lingnert et al., 2002). The extent and rate of the reaction is modified by a number of factors such as temperature, pH, moisture level, oxygen, metals, phosphates, sulphur dioxide and other inhibitors, and these interactions can be complex. For example, the use of monocalcium phosphate in both cookies and crackers aids the Maillard reaction by providing phosphate which catalyzes the reaction NS contributes to lowering of the pH which assists in the provision of reducing sugars, but also slows the reaction by moving the pH to less favourable acidic conditions.

Caramelization occurs above 120°C as sugars are dehydrated and eventually condense or polymerize into a large variety of complex molecules which contribute to both flavour and colour (Purlis, 2010). Sucrose is hydrolyzed to glucose and fructose, which degrade to other compounds, e.g. osuloses; however, the yellow-coloured hydroxymethylfurfural (HMF) is a key product, the reaction kinetics of which have been modelled and related to colour development (Quintas, Branda, & Silva, 2007). The darker brown colours of caramelization are proposed to occur as a result of HMF and furfural polymerizing

(Kroh, 1994). Unlike the Maillard reaction, caramelization proceeds more rapidly at extremes of pH ($9 < \text{pH} < 3$) (Kroh, 1994).

2.4.3 Alteration of chemical composition

Key chemical changes occurring in cookie and cracker dough during baking, such as those associated with leavening and the development of colour and flavour, have been addressed. These lead to the development of product attributes desirable to consumers. One change in composition of concern for health reasons, and therefore undesirable to consumers, is the development of acrylamide (AA) which has been identified in food since 2002 (Swedish National Food Administration, 2002). Carcinogenicity of AA in rats was demonstrated when spiked drinking water increased the incidence of tumors (Friedman, Dulak, & Stedham, 1995). Although later epidemiological studies concluded no positive association between dietary AA and cancer risk in humans (Mucci & Adami, 2009), it may be involved in carcinogenesis via pathways other than genotoxicity (Hogervorst, Schouten, Konings, Goldbohm, & Van den Brandt, 2009).

The highest levels of AA occur in potato crisps ($1496 \cdot 10^{-9}$), baked and fried potato products ($424 \cdot 10^{-9}$), breakfast cereals ($220 \cdot 10^{-9}$), crisp breads ($300 \cdot 10^{-9}$) and bread ($30\text{-}50 \cdot 10^{-9}$) (Tareke, Rydberg, Karlsson, Eriksson, & Tornqvist, 2002; Svensson et al., 2003; Becalski, Lau, Lewis, & Seaman, 2003). A number of paths for AA formation are reported; however, the main route of AA formation in food is as a result of the Maillard reaction (Claeys, De Vleeschouwer, & Hendrickx, 2005). Labeled amino acids heated with glucose showed asparagine to be the most important amino acid in AA formation (Becalski et al., 2003). The positive effect of sugars (fructose, glucose and sucrose) and

asparagine on AA concentration was shown in French fries (Becalski et al., 2004).

Acrylamide formation is dependent on temperature in low-moisture (<4%) systems, e.g. starch model systems and flatbreads, with maxima occurring at 190-210°C (Brathen & Knutsen, 2005). Formation in higher moisture products (bread crust) continued to increase with increasing temperature, and a strong positive correlation between temperature (200-260°C) and AA has been shown during baking of white bread (Ahrné, Andersson, Floberg, Rosén, & Lingnert, 2007).

As most AA in foods occurs as a result of the Maillard reaction, and the Maillard reaction rate is determined by pH, the rate and extent of AA formation can be controlled by modifying pH (Claeys et al., 2005). Acrylamide levels were maximized at pH 8 in potato cubes, while formation was shown to slow and degradation increase when pH was lowered to ~6 (Rydberg et al., 2003). Acrylamide also can be mitigated by controlling precursor concentration. Fructose and glucose are efficient precursors to AA formation when added to homogenized potato, although at high levels AA development was reduced, possibly due to the sugars' affinity for water inhibiting pyrolysis reactions (Rydberg et al., 2003). Asparagine can be reduced using asparaginase that hydrolyzes it to aspartic acid. This reduces AA in products made from dough by up to 90% (Kukurová, Morales, Bednáriková, & Ciesarová, 2009) and has been shown to be effective as a topical application on French fries and potato crisps, where it reduced AA by 60-85% and 60%, respectively (Hendriksen, Kornbrust, Østergaard, & Stringer, 2009). Asparaginase is used in the US for AA reduction, and was approved by Health Canada for use as a food additive in bread, flour and whole wheat flour and foods including baked goods in March, 2012.

Much of the literature concerning dough transformation in baking is based upon lab-scale models, which are extrapolated to real world situations. In this study we begin by profiling the baking characteristics of industrial ovens and then use the data to explain the changes observed in dough derived from those same lines. By characterizing changes in two types of low-moisture snacks (crackers and cookies) and examining the matrix of process inputs from industrial ovens at multiple points during baking, we expected to obtain a better understanding of the outlined dough transformations than a benchtop system would allow.

Chapter 3 Physicochemical Changes of Cookies Baked in an Industrial Oven

3.1 Introduction

A number of parameters can be measured from baked short-dough cookies that are of critical importance to the determination of their quality. Some of these parameters can be assessed on-site with cookies removed from the baking line; however, others must be assessed in a lab. Those parameters that can be easily assessed on the factory floor immediately at the end of the baking process include physical dimensions such as cookie length, width and height, along with measures of colour (typically an assessment of lightness). These values provide direction for on-the-fly process adjustments by operators and are essential to maintaining product quality. Other parameters however are not commonly assessed on-site during production, due to time constraints, expense, or because of the requirement for specialized equipment. The determination of AA content, which has become increasingly important since its discovery in baked goods (Rosen & Hellenas, 2002), is one such example.

In lieu of conducting multiple tests at the end of every bake line, modelling of baking processes may be used to understand how to positively influence product characteristics while also providing a valuable tool for predicting product quality. Modelling has proven useful with regard to explaining both structure and colour development in baked short-dough (Chevallier, Della Valle, Colonna, Broyart, & Trystram, 2002). In particular, the elucidation of the roles of sugar (Kweon et al., 2009),

flour constituents and fat (Pareyt & Delcour, 2008) as they influence cookie quality will be important to the development of future baking models. Examination of these models demonstrates how interconnected product formulation, the kinetics of product temperature increase, and moisture content are to product quality indicators such as surface colour, and thickness (Broyart & Trystram, 2003). However, attempts to mimic industrial processes at the benchtop or pilot oven scale have highlighted the difficulties of replicating the conditions inside even a single section of an industrial tunnel oven, as factors such as the contribution of oven walls to heat transfer are difficult to estimate accurately (Boulet, Marcos, Dostie, & Moresoli, 2010). Further complications arise when comparing models to industrial ovens that can differ greatly in their characteristics. Tunnel ovens may differ in length, run at different conveyor speeds depending upon the product being made, and have multiple zones, each with discrete characteristics of temperature, humidity, and airflow. As the current study was an examination of how short-dough cookie characteristics develop throughout the baking process, it was decided to use a commercial dough formulation subjected to an industrial baking process rather than a modelled or benchtop approach. This provided an opportunity to place thermo-chemical events, such as the generation of AA, and product colour change, into a real-world timeline, that may present opportunities to mediate or otherwise modulate their development.

3.2 Materials & Methods

3.2.1 Cookie Dough

The cookie dough used in this study was a proprietary commercial formulation having a publically-available ingredient declaration as follows: enriched wheat flour, shortening, sugar, syrup, wheat bran, malt and corn extract, butter, milk powder, salt, sodium bicarbonate, wheat or corn starch, ammonium bicarbonate, and artificial flavour. Sugar, water, and fat content in the formulation were 16%, 10%, and 21% (d.b.), respectively.

3.2.2 Cookie Quality Measurements

Dough and cookie samples were collected from five points throughout the process: from the conveyor immediately prior to entering the oven (dough), via three ports in the side of the oven situated at 13.4, 27.1 and 47.5 m from the entrance, and at the oven exit (61 m). Excluding the dough sample, these sampling points corresponded to the following sampling times and oven air temperatures: 89 s and 179°C, 181 s and 175°C, 317 s and 217°C, and 406 s and 148°C. One set of samples was submerged immediately in liquid nitrogen to arrest any further physical or chemical changes. These were then packed into plastic freezer bags and stored at -20°C for further analyses. A second set was taken to an on-site laboratory where they were evaluated after 30 minutes.

Internal Product Temperature

Internal temperature was assessed using a thin, type-T thermocouple inserted horizontally into the dough. The thermocouple was attached to a modified Scorpion[®] humidity data logger (Reading Thermal Systems, Reading, PA) via a product probe

interface (PPI). The data logger was set to record temperature data every two seconds throughout oven transit. Internal temperature measurements were taken as close as possible to the middle of a timed production run to ensure the oven conditions had equilibrated. Internal product temperatures are shown for the five oven sampling points (Figure 3.1).

Cookie Dimensions

Cookie dimensions as determined by width (the distance from side to side of the cookie at a right angle to the direction of travel i.e. across the belt) and length (the distance across the cookie in the direction of travel) were measured using electronic callipers (TOP Craft, Globaltronics GmbH & Co.) immediately upon removal from the oven. Five measurements were taken at each of the five sampling points. Measurements of height were collected in association with compression measurements using a TA.XTplus Texture Analyzer (Stable Micro Systems Ltd., Surrey, UK). A minimum of five height measurements were collected for each sampling point.

Colour

L* values were gathered on site using a Hunter colour meter (Hunter Associates Laboratory, Inc., Reston, VA, USA). Measurements were obtained by placing 12 cookies top-down into a rotary sampling chamber and overlaid such that there were no gaps between them. The sampling chamber was rotated 90° three times with the L* value being measured each time. The reported colour meter values were means of these three measurements.

Instrumental Texture Evaluation

Instrumental assessments of cookie texture were carried out using a TA.XTplus Texture Analyzer (Stable MicroSystems). Compression testing was performed on samples starting with the dough, through to those from the oven exit. The rig for this test was a 6-mm cylinder probe, and test settings were: pre-test speed at 2 mm/s, test speed at 1 mm/s and distance at 1.3 mm. A 5-kg load cell was used and the maximum compression force, based on the average of three replicates, was reported. For the bend force test, a three-point bend rig was utilized, and testing was carried out on samples from port 2 of the oven only, since the earlier samples were too soft. The following settings were used for this test: the distance between the supports was 25 mm, pre-test speed at 3.0 mm/s, test speed at 3.0 mm/s, and distance at 5 mm. A 5-kg load cell was used and the maximum bend force, based on the average of three replicates, was reported.

Pasting Properties

The pasting parameters of each treatment of cookies were assessed using a Rapid Visco Analyser (RVA-4™, Newport Scientific Pty. Ltd, Warriewood, NSW, Australia) applying the Standard 2 method and data were analyzed in Thermocline for Windows (TCW3) software. Samples collected from port 3 and the exit were ground using a mortar and pestle. As the higher moisture of less-baked samples prevented effective grinding, these were crumbled by hand while frozen. All treatments were mixed with DI water in a RVA canister on a 10.7% dry-basis to achieve 28 g total weight and allowed

to hydrate for 1 hour prior to testing. At least two pasting curves were collected for each treatment and the means of these replicates were reported.

Thermal Properties

The thermal properties of cookie dough and fully-baked cookies (Exit) were assessed using a Differential Scanning Calorimeter (TA Q1000, TA Instruments, New Castle, DE). Samples were weighed into alodined aluminum pans 1:3 (w/w) with DI water, sealed and left to equilibrate for 24 hours at room temperature. Heating proceeded at 5°C per minute from 25 to 120°C, followed by cooling at 5°C per minute to 25°C. An empty pan was used as a reference. Onset temperature (T_o , °C), peak temperature (T_p , °C), conclusion temperature (T_c , °C) and gelatinization enthalpy (ΔH , J/g) were determined using Universal Analysis 2000 software (TA Instruments, version 4.7A).

Microscopy

Bright-field and polarized light microscopic examinations to evaluate birefringence, were conducted on dough and fully-baked cookies using an Olympus BX60 Microscope (Olympus Optical Co. Ltd., Japan) at 40x magnification. Images were captured using an attached Olympus DP71 camera and were analysed using ImageProPlus software (Media Cybernetics, Inc., Bethesda, MD, USA). Samples were prepared by being ground and sieved as for the RVA method and a 0.1 g-sample of each was suspended in 3 mL of DI water. A 5- μ L subsample was mixed with 5- μ L of 0.02% iodine to stain.

Moisture Content

Moisture content of all treatments was assessed using an Ohaus MB45 moisture balance (Ohaus Corporation, Parsippany, NJ, USA). A 1-g sample was ground by mortar and pestle into the moisture balance pan and the balance was programmed to run at 130°C for 3 minutes. Mean values of five replicate measurements taken from each treatment were reported.

Water Mobility

A Bruker mq20 Series NMR Analyzer (Bruker, Milton, ON, CA) was used to carry out proton relaxation analysis on samples of dough and fully-baked product. Spin-spin (T_2) relaxation measurements were determined using a Carr-Purcell-Meiboom-Gill (CPMG) sequence with the following parameters: $P_{90}=2.78 \mu\text{s}$ and $P_{180}=5.56 \mu\text{s}$ were the pulse width, dead time = $9 \mu\text{s}$ before and after applying the pulse; recycle delay= 5 s between scans; 8 scans and 256 echoes were completed. An inverse Laplace transform was applied to the CPMG sequence to quantitatively analyze the pulsed NMR sequencing using the CONTIN application with Minispec software version 2.3 (Bruker). Measurements were performed in triplicate.

AA Development

AA measurements were carried out on all treatments using cookies that had been immediately frozen in liquid nitrogen. Extraction and analysis were adapted from the Zeng et al. (2010) method for assessment of AA in fried potato strips with the following modifications: the initial hexane wash for surface oil was removed and the sonication

step was substituted with homogenization. A 1-g sample was thoroughly homogenized with 10 mL of DI water at high speed for 1 minute using a Powergen 125 homogenizer (ThermoFisher Scientific, Waltham, MA, USA). A 7-mm flat-bottom generator was used. The concentration step to 1 mL was carried out at 50°C under N₂.

GC–MS analysis was performed on a Thermo Scientific DSQ™ Single Quadrupole GC/MS. Separation of the reaction products was on a Thermo Scientific TG-WaxMS column (30 m x 0.25 mm ID, 0.25 µm film thickness). Helium at a flow rate of 1 mL/minute was used as the carrier gas. The injection volume was 2 µl PTV split, with a split flow of 10 mL/minute and a split ratio of 10. The injector was operated at an inlet temperature of 220°C. The oven temperature programme was as follows: 0 to 5 minutes hold at 130°C, ramp at 10°C/minute to 200°C, ramp at 20°C/minute to 250°C, and hold at 250°C for 10.5 minutes. Selective ion monitoring (SIM) was used for the detection of the AA derivative, 2-BPA starting at 10.5 minutes and ending at 12 minutes. The ion monitored for 2-BPA was m/z 149.

3.2.3 Isolated Starch Attributes

Starch Isolation from Cookie Dough

In order to assess starch properties without interference from cookie components such as sugars or lipids, starch was isolated using the following procedure adapted from Marti, Pagani, & Seetharaman (2011):

Samples (10 g) were broken up (dough) or ground with mortar and pestle (cookies) and stirred with 100 mL of DI water for 5 minutes. These were centrifuged at 6000 rpm for 5 minutes at 15°C and the supernatant was discarded. Protein extraction buffer (12.5 mM

sodium borate buffer adjusted to pH 10.0 and consisting of 0.5% SDS and 0.5% Na₂S₂O₅) was added in a w/v ratio of 1:20 and stirred for 5 minutes. Samples were again centrifuged, the supernatant discarded, and the wash with protein extraction buffer and centrifugation was repeated. The residue was then washed three times with DI water including a centrifugation step. Following this the residue was suspended in 100 mL of DI water and the slurry was passed through four layers of cheesecloth and then through a 70 µm nylon mesh. The filtered residue was centrifuged and suspended in 100 mL of protease solution containing 0.50 g of trypsin from porcine pancreas (13,000-20,000 BAEE units/mg protein; Sigma-Aldrich) and 0.25 g of papain from *Carica papaya* (≥3 units/mg; Sigma). Following overnight incubation at room temperature with magnetic stirring, the residue was washed three times with DI water and twice with ethanol (95%). Isolated starch was then washed with acetone and left to dry overnight. Once dried the starch was ground by mortar and pestle for further analysis.

Pasting Properties

The pasting parameters of starch isolated from dough and fully-baked cookies was assessed using the method as outlined for cookies and with treatments being mixed with DI water on a 7.4% dry-basis.

Thermal Properties

The thermal properties of the isolated starches were assessed using the method as outlined for cookies but with heating proceeding at 5°C per minute from 25 to 120°C.

Crystallinity

Wide-angle X-Ray Powder Diffraction measurements were conducted on isolated starch samples (~0.1 g) from cookie dough and fully-baked cookies (Exit) using a Rigaku Powder Diffractometer (Rigaku Co., Tokyo, Japan). CuK α 1 radiation ($\lambda = 1.54 \text{ \AA}$) was selected using a quartz monochromator. The diffractometer settings were: current, 40mA; voltage, 40kV; scan speed, 1° per minute; range, 3-35°, 2 Θ ; and sampling width, 0.02°. Data were smoothed using Jade 6.5 software and were normalized to equal total scattering in the 3-35° 2 Θ range. Peaks were fitted to the diffractograms and their position, area and width assessed using Igor Pro software (WaveMetrics, Inc., Version 6.0.5.0).

3.2.4 Data Analysis

Data were subject to analysis of variance (ANOVA) using Proc GLM to account for data sets of variable size. Significant differences between treatments were established using Tukey's HSD (Honestly Significant Difference) with significance set at $p < 0.05$. All analysis was conducted using SAS 9.2 (SAS Institute Inc., Cary, NC, USA).

3.3 Results & Discussion – Cookies

3.3.1 Dimensions

The influence of heat and the action of leavening agents are key to the changes in dimensions that occur when cookies are baked. Heat warms the dough and melts the fat component, conferring plasticity to the dough and allowing it to flow more easily. This

results in an initial spreading. Initially cookie width and length increased significantly as product temperature increased, with maximum values in samples taken from port 2 (Table 3.1). From this point onwards, length and width reduced as baking progressed, with significant contraction evident by the end of the process. In addition, cookie height increased significantly between ports 2 and 3, after which it remained unchanged (Table 3.1). Height increased due to heat and the action of leavening agents. Heating of dough leads to an increase in water vapour pressure and expansion of trapped air bubbles by approximately 1.25 times (Matz, 1992). In this case, the chemical leavening agents used (sodium bicarbonate and ammonium bicarbonate) would have been responsible for the majority of height increase by release of CO₂. Figure 3.1 summarizes these changes in cookie dimensions throughout baking using the derived terms diameter and volume.

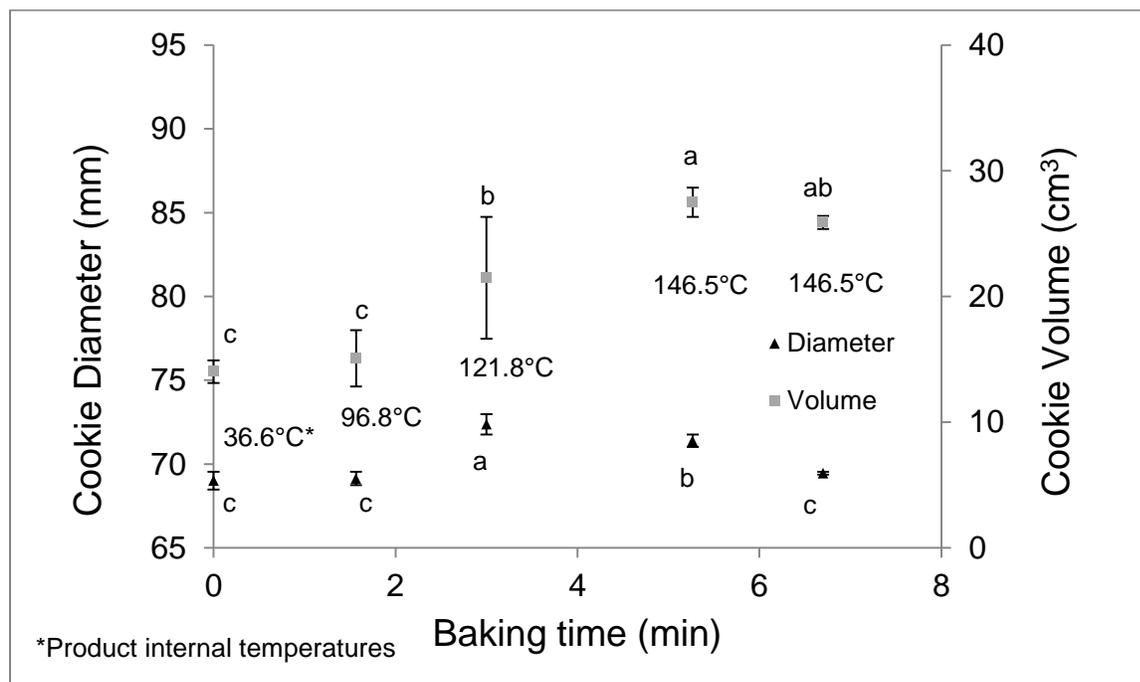


Figure 3.1 Cookie volume and diameter during baking*

The changes observed in this study followed a pattern of expansion and setting previously documented in modelled sugar-snap (AACC 10-52) cookies (Miller & Hosney, 1997). However, this differs from data for industrially-produced, short-dough cookies (Chevallier et al., 2002) because of differences in the formulation and baking conditions for the two cookie types. Protein interactions also have been implicated in contributing to structural and textural attributes of cookies; for example Pareyt, Van Steertegem, Brijs, Lagrain, & Delcour, (2010) reported an increasing resistance to collapse due to gliadin-glutenin crosslinking, while Chevallier et al., (2002) suggested that protein aggregation alone was insufficient to prevent collapse during baking. Thus, the relative contributions of each dough component towards structural development are

difficult to quantify and compare due to differences in formulation, baking conditions, or both, between different studies.

3.3.2 Colour

The development of colour, i.e. browning, in cookies is the result of two simultaneously occurring processes, the Maillard reaction where sugars interact with amino acids, and caramelization which is a direct degradation of sugars (Zanoni, Peri, & Bruno, 1995). Prior to browning, cookies are known to become lighter in colour due to surface drying of the dough (Shibukawa, Sugiyama, & Yano, 1989; Chevallier et al., 2002). L*-values obtained (Table 3.1) showed that partially-baked cookies at port 2 were lighter than the starting dough. Subsequent browning reactions led to darkening of cookies from port 3 onwards. Browning has been shown to occur in crackers, a similar low-moisture baked-product, upon reaching a critical temperature of 105-115°C (Broyart, Trystram, & Duquenoy, 1998). While this temperature range occurred between ports 1 and 2 in the current process, a corresponding drop in L* values was not observed until port 3. Such a delay between initiation of the browning process and observed browning was expected due to the complexity of factors, apart from temperature, influencing the Maillard reaction and caramelization, including product formulation, humidity in the oven, and product water activity (Purlis, 2010). Of these, product formulation was important for providing a relatively abundant source of starting material for browning reactions to proceed, such as proteins, sugars, syrup, mono- and di-saccharides, and milk powder.

3.3.3 Instrumental Texture Evaluation

Compression

In the current study, there was a significant increase in cookie firmness between samples from the oven entrance and those taken from port 1 (Table 3.1). This increase was influenced by the sampling and measurement procedure, i.e. the hot product was cooled before texture measurement and it is likely that the partially cooked dough set to a firmer structure upon cooling. Assessment of the cookies sampled from port 2, however, showed the firmness to have returned to a level not significantly different from that of the dough at the entrance. As cookies sampled from port 2 had spent a longer time in the oven, they would be expected to have a more developed set structure upon cooling. However, these had also increased significantly in length and width.

Compression testing beyond port 2 showed a steady increase in firmness, as would be expected due to the development of the hard-set structure that is characteristic of fully-baked cookies and accounted for by sugars melting during baking and reforming in the glassy state (Chevallier et al., 2002).

Three-Point Bend

Results of the 3-point bend test also reflected the development of cookie structure seen in compression testing. Cookies sampled from port 2 represented the earliest point at which this method could be successfully conducted due to the dough's plasticity in the earlier stages of baking. Between port 2 and port 3, and port 3 and the exit, the amount of force required to fracture the cookie samples increased significantly with baking time (Table 3.1). Increasing values from the 3-point bend test have been related to the

development of crispness in cookies during baking, an important attribute resulting from the formation of a spongy structure in the initial stages of baking and a subsequent decrease in moisture content (Piazza & Masi, 1997).

Table 3.1 Instrumental measurements of cookie dough throughout the baking process

Location	Entrance	Port 1	Port 2	Port 3	Exit
Width (mm)	69.3c ¹	69.5c	72.9a	71.9b	68.5d
Length (mm)	68.7c	68.8c	71.9a	70.9ab	70.5b
Height (mm)	3.9b	4.2b	5.2b	6.8a	6.8a
Colour (L*)²	57.2	54.3	63.6	55.2	54.5
Compression (g)	2488.4c	4799.1b	1841.1c	2703.7c	6065.4a
3 Point Bend (g)	-	-	134.6c	580.5b	1174.0a
Internal Temperature (°C)	36.6	96.8	121.8	146.5	146.5
Moisture (%)	16.4a	15.9a	14.0b	8.4c	3.6d
NMR T₂ (2) (ms)	40.1a	35.6ab	32.3b	22.1c	22.5c
AA (10⁻⁹)	Below detection threshold	Below detection threshold	Below detection threshold	26.7b	55.3a

¹Means followed by the same letter in each row are not significantly different at 95%

²Colour meter values obtained on site were means of 3 reps from a combined 12 cookie sample at each location; as such these were not appropriate to subject to ANOVA.

3.3.4 Pasting Properties

Pasting temperatures were very similar between treatments (Table 3.2). Despite the presence of sugar in the cookies, this did not result in a significant increase in pasting temperature onset. Sugars constituted only 1.8% by weight in the RVA sample mixtures; pasting temperature has been shown to increase when there is a much greater proportion of sugar, e.g. 50% w/w sugar solutions (Kweon et al., 2009).

Other pasting parameters that showed no significant differences between treatments included peak, trough, and final viscosities. Only two parameters showed significant differences. Breakdown for fully-baked cookies was significantly lower than for all other treatments, and setback for fully baked cookies was significantly lower than for dough and cookies sampled from port 1 (Table 3.2).

Table 3.2 Pasting parameters of samples throughout baking as measured using a Rapid Viscoanalyzer

Location	Entrance	Port 1	Port 2	Port 3	Exit
Pasting temperature measured (°C)	85.0ab ¹	85.8a	86.0a	84.7b	Not quantifiable
Peak (Pa.s)	0.255a	0.276a	0.294a	0.314a	0.234a
Breakdown (Pa.s)	0.045a	0.067a	0.061a	0.052a	0.002b
Trough (Pa.s)	0.211a	0.209a	0.233a	0.263a	0.233a
Setback (Pa.s)	0.333a	0.334a	0.263ab	0.291ab	0.230b
Final Viscosity (Pa.s)	0.544a	0.543a	0.496a	0.554a	0.463a

¹Means followed by the same letter in each row are not significantly different at 95%

3.3.5 Thermal Properties

Thermograms (DSC) of cookie dough (Entrance) and fully-baked (Exit) samples each featured two events upon heating, an initial endotherm due to starch gelatinization, followed by a smaller endotherm indicating melting of the amylose-lipid complex (Slade, Levine, Wang, & Levoella, 1996). An exothermic event observed during cooling (81-71°C) was attributed to the reversing of the amylose-lipid complex transition. No significant differences were observed between the cookie dough and fully-baked cookies for any of the parameters (To, Tp, Tc, or ΔH). This was in line with DSC measurements of flour starch and starch from cookies made with the same flour by Kulp, Olewnik, & Lorenz, (1991), that showed no differences in enthalpy parameters, and suggested no change had occurred in the starch during baking.

3.3.6 Microscopy

Micrographs of the dough showed intact A- and B-type starch granules (Figure 3.2a)

which exhibited birefringence when examined with polarized light (Figure 3.2b). Most

micrographs of fully-baked cookies showed features identical to those of the dough.

However, in a small number of cases some differences were observed. An example is

shown (Figure 3.2c) which features intact B-type granules and a mixture of intact and

damaged A-type granules. When examined with polarized light most of the granules in

the fully-baked cookies still produced a Maltese cross pattern; however some of the A-

type granules were found to be only partially birefringent (Figure 3.2d). The observed

loss of birefringence was similar to that seen in a proportion of starch from pasta that

had undergone high temperature drying processes (Guler, Koksel, & Ng, 2002).

Although the amount of available water in these cookies was low, it was apparent that in

some limited instances some starch was damaged during this short-time, high-

temperature process.

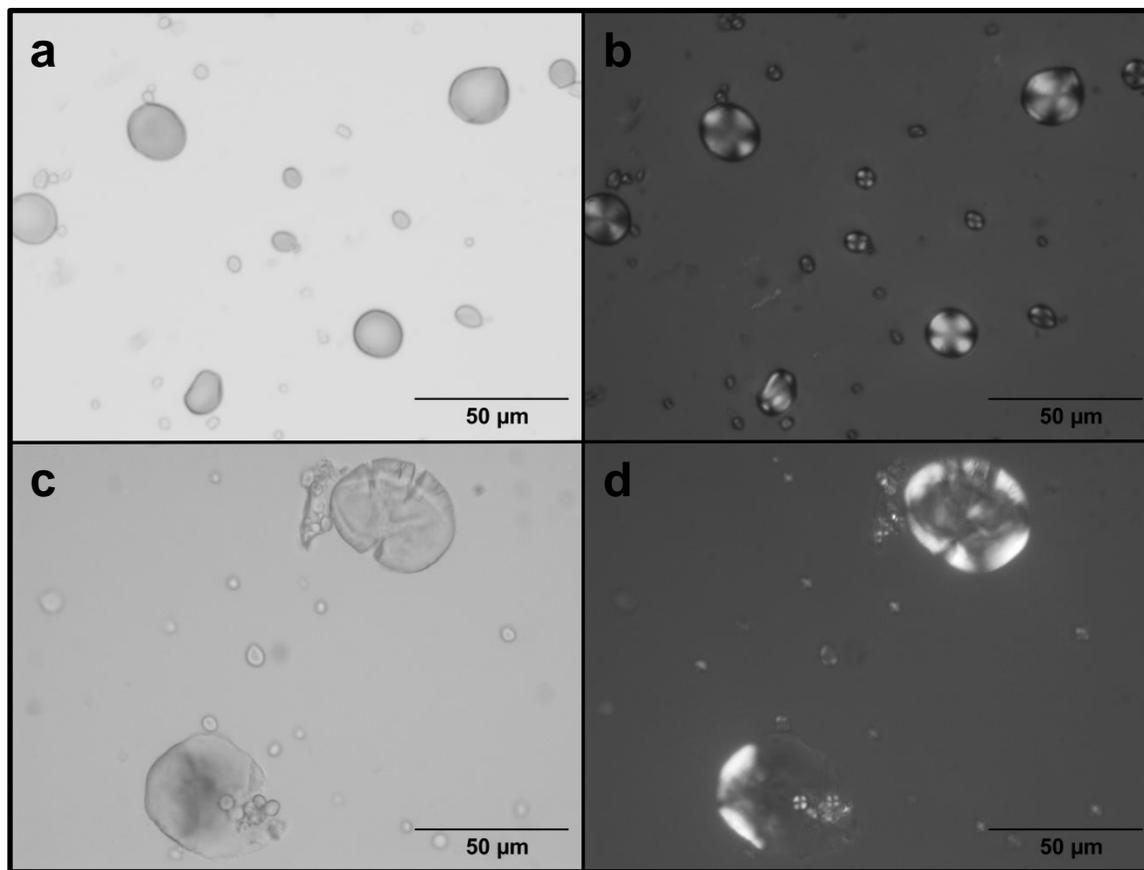


Figure 3.2 Selected light micrographs of cookies highlighting damage to starch granules (For each sample, bright field is on the left and the same field between crossed polarizers is on the right. A & B = dough, C & D = fully-baked cookie)

3.3.7 Moisture

During the initial warming stage from the oven entrance through to port 1, there was no significant change in moisture content of the dough. However, at each subsequent sampling point through to the exit the moisture content decreased significantly (Table 3.1). Most of the water present was vaporized, contributing to leavening, and resulting in a drier and less dense product (Chevallier, Colonna, Buleon, & Della Valle, 2000).

3.3.8 Water Mobility

The distribution of T_2 proton relaxation times for cookie dough produced a three-peak plot (Figure 3.3). The mean values of T_2 (1) = 5.4 ms, T_2 (2) = 40.1 ms and T_2 (3) = 119.3 ms obtained for the dough were similar to those reported previously for cookie dough (Assifaoui, Champion, Chiotelli, & Verel, 2006a; Goldstein & Seetharaman, 2011). As such it seems most likely that the T_2 (1) peaks identified corresponded to protons from intragranular water in the starch and the T_2 (3) peaks to protons in the oil component, while the T_2 (2) peaks represented protons from extragranular water in association with starch and sucrose. Similarly long T_2 constants corresponding to relatively mobile water molecules in dough have been shown to decrease during starch gelatinization as proton interactions with macromolecules increase (Kim & Cornillon, 2001). Cookie internal temperature increased from 37 to 97°C by the time the cookies were sampled from port 1, although there was no significant decrease in T_2 (2) to suggest gelatinization had occurred. Microscopic examination of the dough at this point also failed to show indications of gelatinization (not shown). However, T_2 (2) did decrease significantly from the beginning to the end of the process with a large decrease occurring between ports 2 and 3 (Figure 3.4). The initially low-moisture content of the dough (16.4%) would have been largely responsible for this lack of starch gelatinization. It has been shown that in a cookie dough (moisture content 17.5%), starch swelling, and not necessarily gelatinization, will occur upon heating (Assifaoui, Champion, Chiotelli, & Verel, 2006b). It is suggested that removal of the easier to remove and more mobile water fraction at the beginning of baking, followed by starch swelling (Figure 3.2), an increase in viscosity of the dough, and increased interactions

between the remaining water and other macromolecules, e.g. sugar, led to the observed decrease in proton mobility.

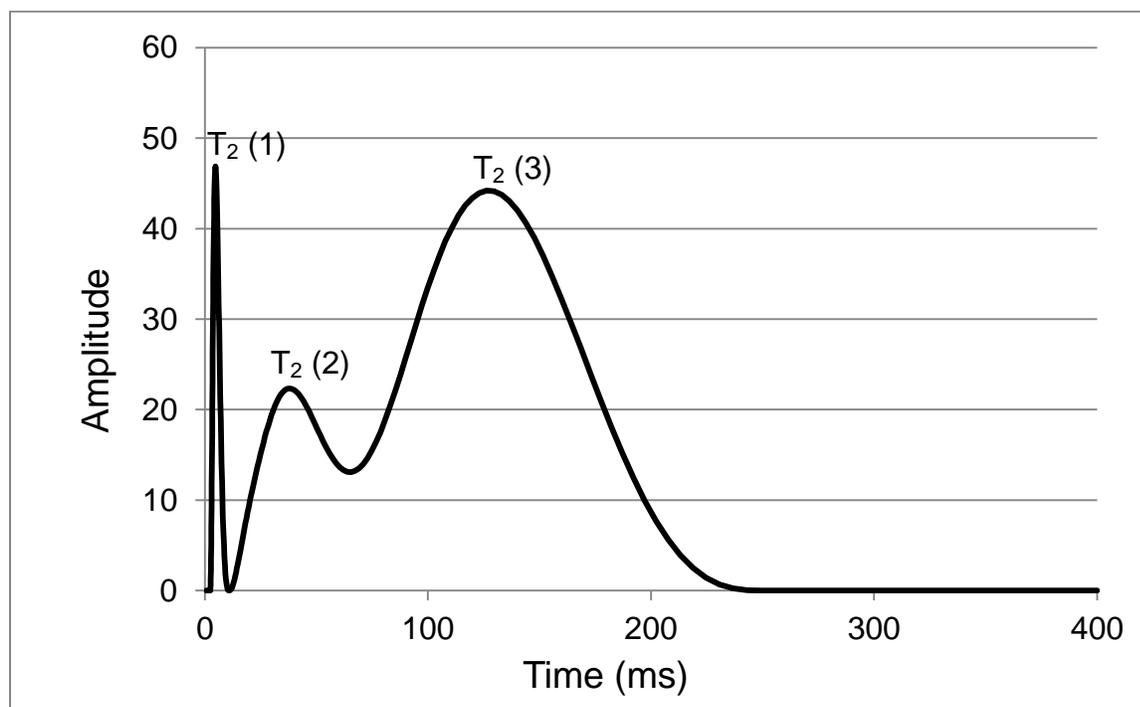


Figure 3.3 Mean T_2 proton relaxation times of unbaked cookie dough

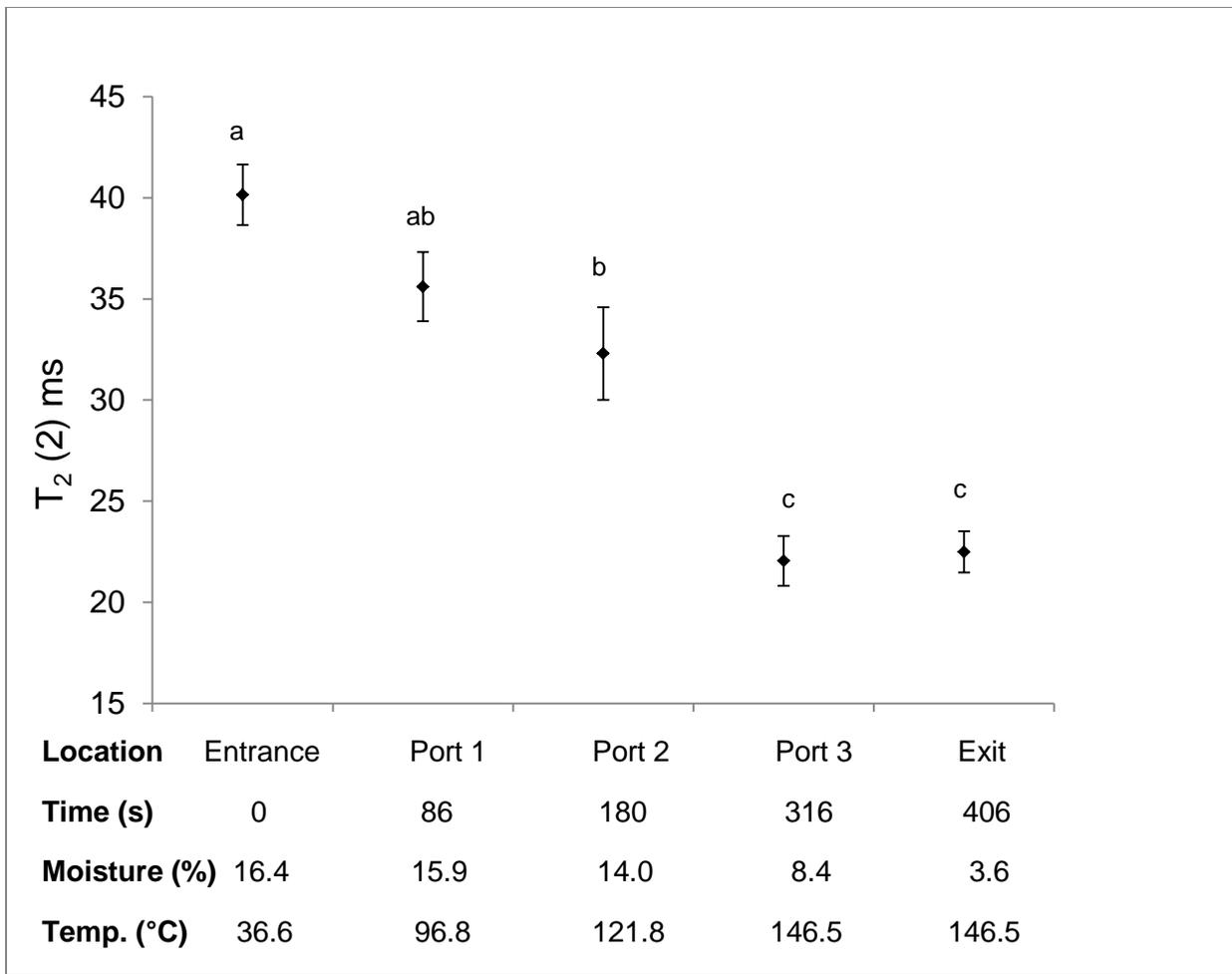


Figure 3.4 T2 (2) proton relaxation times as cookies are baked

3.3.9 AA Development

Acrylamide was first detected in samples taken from port 3 of the oven (26.7×10^{-9}) and was present at a significantly greater concentration in the final product (55.3×10^{-9}). While some AA would have been formed prior to port 3, there were no quantifiable peaks observed above the background noise in GC traces from earlier samples. The level of AA found in these cookies fell between the values that have been published for crackers (30×10^{-9}) and biscuits (120×10^{-9}) as determined in an earlier survey of baby food products (Health Canada website, 2009). As expected, the appearance of AA closely followed the development of browning reactions in the cookies (Becalski, Lau, Lewis, & Seaman, 2003). It has been noted that in a number of systems, including a starch model, a freeze-dried flat bread dough and a flat bread, that the formation of AA goes through a maximum at temperatures of 190-210°C (Brathen & Knutsen, 2005). While the internal temperature of the cookies at port 3 was 146.5°C, the air temperature of the oven immediately above the oven band at the same point was 192°C, implying a cookie surface temperature highly conducive to AA formation. Also of note is that the majority of colour development in the cookies, corresponding to a reduction in L* value, had already occurred by the time the cookies were assessed at port 3, while the level of AA generated at this point was only just detectable. When assessed at the exit, colour was incrementally darker, yet the concentration of AA was significantly increased.

3.4 Results & Discussion – Starch

3.4.1 Pasting Properties

RVA evaluation of starch isolated from dough and from fully-baked cookies (Figure 3.5) showed differences of a greater magnitude in pasting properties than in the context of the cookies (Table 3.2), allowing a clearer assessment of an apparent heat-moisture-treatment (HMT)-like effect of baking on starch. There were no significant differences between starch isolated from dough and from fully-baked cookies for pasting temperature and peak value. However, starch from fully-baked cookies was significantly different from starch extracted from the dough for each of the remaining parameters, i.e. lower breakdown, higher trough, higher setback and higher final viscosity (Figure 3.5). HMT at values of 25% moisture and 110°C has been shown to produce similar effects in a sweet potato starch, albeit with an associated increase in pasting temperature and a slight decrease in peak value (Collado & Corke, 1999). As aggregation of amylose on cooling leads to gel formation, it is suggested that baking had a HMT-like effect in this case and facilitated greater amylose leaching. This contributed to the observed effects in starch from baked cookies, particularly the significantly greater final viscosity on cooling. Increased leaching of amylose from wheat starch upon heating has been previously described (Hoover & Vasanthan, 1994) and related to increased gel viscosity (Jacobs, Eerlingen, Clauwaert, & Delcour, 1995).

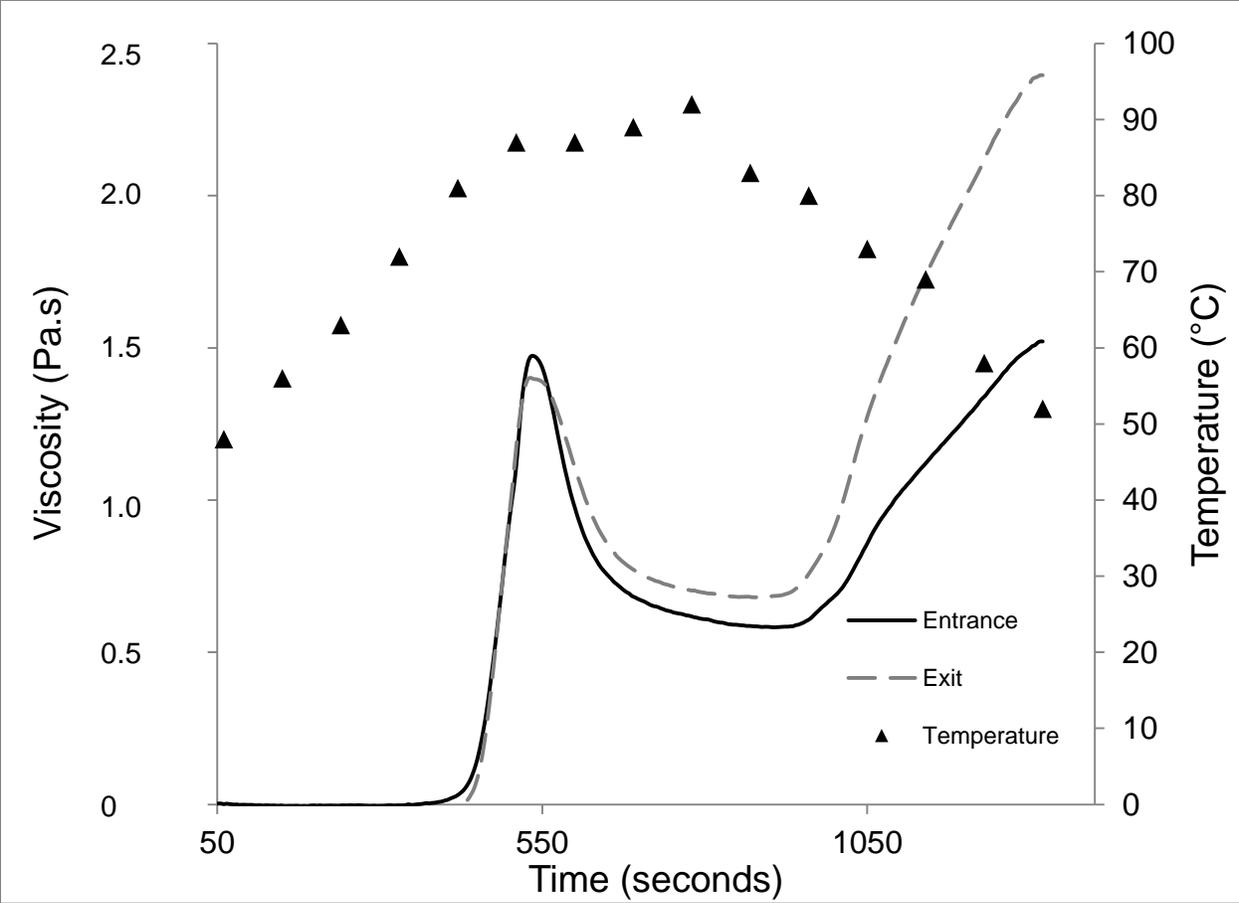


Figure 3.5 RVA™ pasting profiles of isolated starch from dough and fully baked cookies at measured temperatures

3.4.2 Thermal Properties

DSC thermograms of the isolated starch samples each featured two endotherms. These were for starch gelatinization, and the amylose-lipid complex transition, respectively. The isolated starches showed a number of significant differences in their measured parameters for both endotherms (Table 3.3). For the starch gelatinization peak, the onset, peak and end temperatures were all significantly upshifted, while there was no associated change in enthalpy. For the amylose lipid complex, there were significant increases in peak onset, peak temperature and enthalpy. These results contradict the earlier DSC examination of starch in the context of a cookie matrix that showed no effect of baking upon starch properties. It is possible that the assessment of starch thermal properties in the context of cookies may have had the effect of masking the differences that were seen in the isolated starches. The effect of sugar on the system was clearly demonstrated by a comparison of the DSC parameters T_o , T_p and T_c (Table 3.4). In that case, a comparison of cookie dough versus isolated starch from cookie dough, and also of fully-baked cookies versus starch from fully-baked cookies, showed the expected upshift in the starch gelatinization endotherm characteristic in the presence of sugar (Mamat et al., 2010)

Table 3.3 DSC parameters of isolated starch at different sampling points during baking

	Endotherm 1 – Starch Gelatinization				Endotherm 2 – Amylose Lipid Complex Transition			
	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)	To (°C)	Tp (°C)	Tc (°C)	ΔH (J/g)
Entrance	52.9d ¹	59.2d	64.8c	11.5ab	88.9b	95.2b	100.0a	1.9c
Std.Dev	0.1	0.1	0.5	0.6	0.1	0.4	1.7	0.2
Port 1	53.5c	58.9d	66.0abc	11.5ab	88.9ab	95.51ab	100.9a	1.9c
Std.Dev	0.1	0.0	0.5	0.1	0.8	0.1	0.0	0.1
Port 2	55.0b	60.3c	65.5bc	11.9a	88.7b	95.0b	100.6a	2.0bc
Std.Dev	0.0	0.0	0.1	0.7	0.3	0.6	0.3	0.1
Port 3	55.4a	62.4a	67.3a	10.5ab	88.7b	95.6ab	101.5a	2.9a
Std.Dev	0.0	0.4	0.5	0.4	0.4	0.1	0.0	0.0
Exit	55.5a	61.5b	66.8ab	9.7b	90.7a	96.8a	102.2a	2.5ab
Std.Dev	0.1	0.1	0.3	0.2	0.4	0.3	0.4	0.2

¹Means followed by the same letter in each column are not significantly different at 95%

Table 3.4 A comparison of DSC parameters for isolated starch versus dough and versus cookie

Endotherm 1 – Starch Gelatinization				
	Dough	Starch isolated from dough	Cookie	Starch isolated from cookie
To (°C)	60.0a ¹	52.9b	60.2a	55.5a
Std.Dev	0.0	0.1	2.3	0.1
Tp (°C)	66.0a	59.2b	65.6a	61.5b
Std.Dev	0.4	0.1	1.2	0.1
Tc (°C)	71.4a	64.8b	71.0a	66.8b
Std.Dev	0.3	0.5	0.4	0.3
ΔH (J/g)²	12.1a	11.5a	10.1a	9.7a
Std.Dev	2.5	0.6	0.3	0.2
Endotherm 2 – Amylose Lipid Complex Transition				
	Dough	Starch isolated from dough	Cookie	Starch isolated from cookie
To (°C)	85.8a	88.9a	87.1a	90.7a
Std.Dev	2.8	0.1	1.5	0.4
Tp (°C)	92.5a	95.2a	93.7a	96.8b
Std.Dev	0.9	0.4	0.7	0.3
Tc (°C)	99.7a	100.0a	99.8a	102.2a
Std.Dev	0.8	1.7	0.7	0.4
ΔH (J/g)²	2.0a	1.9a	2.1a	2.5a
Std.Dev	0.9	0.2	0.9	0.2

¹ For each DSC parameter, means followed by the same letter within each pair (dough versus isolated starch, and cookie versus isolated starch) are not significantly different at 95%

²ΔH values for dough and cookies estimated based on starch being 75% of the flour component of formulation

3.4.3 Crystallinity

X-Ray diffraction measurements were made of starch isolated from the dough (Entrance) and from the Exit, i.e. fully baked samples, in order to assess whether baking had any effect on starch crystallinity.

Comparison of the peak position, area and width showed no significant differences in any of these parameters between samples (Figure 3.6).

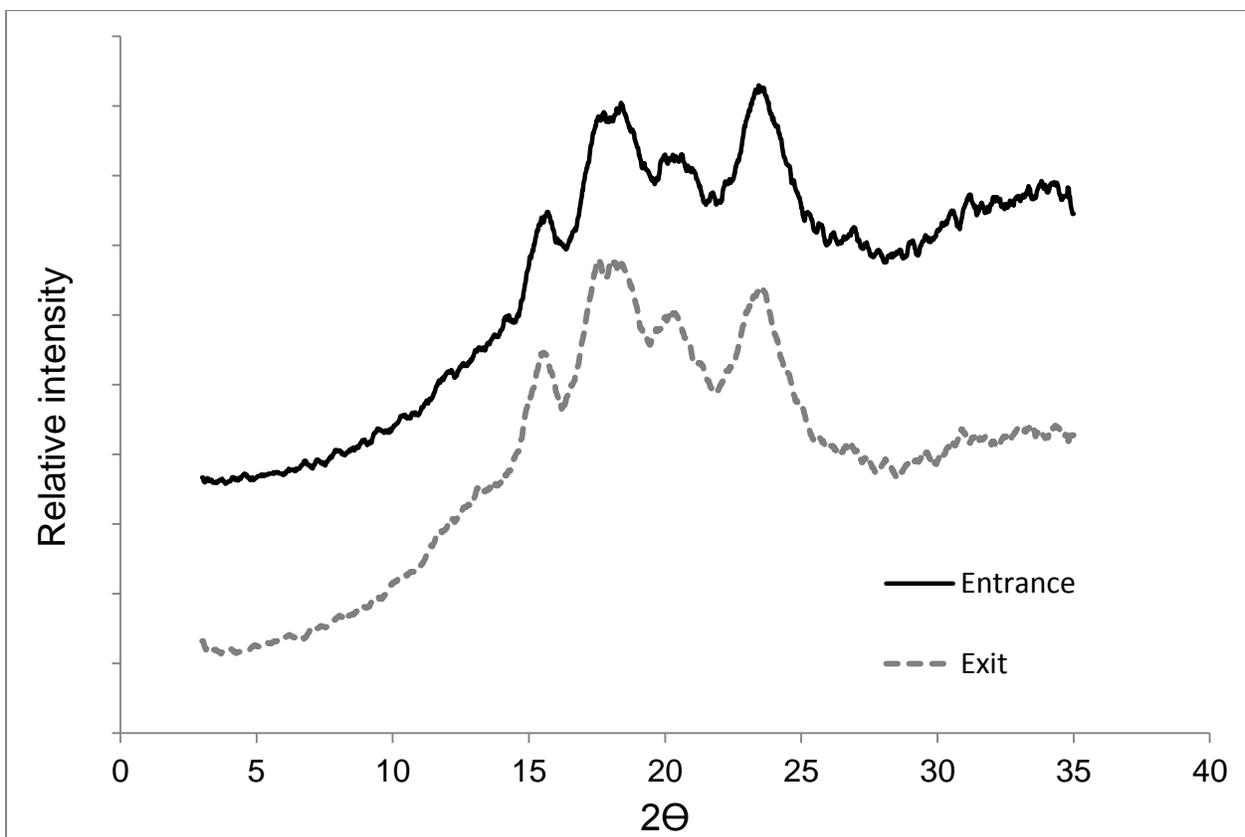


Figure 3.6 X-Ray diffractograms of peak intensities of starch isolated from cookie dough and baked cookies. The graphs are offset for clarity

3.5 Conclusions

The objective of this study was to understand the effects of baking in an industrial tunnel oven on the physicochemical properties of commercially-formulated, short-dough cookies. Due to the complexity of both the process and the formulation used, the focus of the analysis was on describing changes occurring to the macro properties of the cookies and the micro properties of the major constituents. As a result, important developments occurring in the dough have been quantified and the timing of these events in the process has been described as they occur in an industrial process for the first time. By electing to focus on major constituents such as starch, we have verified, in the case of a low-moisture, high-fat and high-sugar product such as cookies, that starch has a role corresponding to filler in such systems, i.e. it occupies space while remaining mostly unchanged. Despite the effectively passive role of starch, the inclusion of flour in cookie formulation also is important for introducing protein which has a role in colour development via Maillard browning. In addition, the transformation of dough into fully-baked cookies was described in terms of processes including the initial lightening prior to browning, the spreading of dough due to melting of fat, the increase in length, width and height due to the action of leavening agents, and the formation of the final set structure. The moisture content was shown to decrease from the entrance through to the exit, with a significantly large drop occurring between ports 2 and 3. This coincided with a significant decrease in T_2 (2) proton relaxation time, demonstrating that as water was removed, only the more tightly-held water was retained. While the majority of starch present was unaffected by baking, its isolation and examination did uncover a number of small but significant changes that pointed to a HMT-like effect of baking on starch

granules. These included partial and full loss of birefringence in a very small proportion of starch granules, the appearance of a disrupted granule border also accompanied by loss of birefringence, and an increase in starch gel viscosity on cooling. Acrylamide formation was shown to closely follow, but lag slightly behind, the development of colour, suggesting that there may be a window in the process where sufficient browning of cookies could be achieved and the level of AA modulated. AA was shown to be present at levels typical of this type of product. Future work in this area will focus on the impact of ingredients that are minor by quantity on product properties, e.g. milk powder which was present in these cookies at <1% was likely to have contributed to browning in conjunction with the sugars present.

Chapter 4 Comparison of a Prototype Oven to an Industrial Snack Cracker Baking Process

4.1 Introduction

During baking of low-moisture dough, a number of transformations are known to occur. These physicochemical changes have been described extensively in the literature (Pareyt & Delcour, 2008; Piazza & Masi, 1997; Purlis, 2010). A common feature of research on baking of low-moisture products is that it is conducted under ideal conditions, either at the lab (benchtop) level, or in a pilot plant. Working under these controlled conditions allows the effects of process inputs, such as oven parameters, and/or product inputs, such as formulation, to be more clearly evaluated for their effects on the baked product. This contrasts with industrial baking, in which oven settings are tightly controlled, yet baking conditions at any given point in a process are not well understood.

Just as scaling up of a process alters its parameters (Sommier, Anguy, Dumoulin, Rojas, & Vignolle, 2011), attempting to scale down a complex process like baking in an industrial oven, and emulating its effects in the lab, presents problems. For example, a method for evaluating the quality of flour used in snack cracker products required a lab-based approach that successfully emulated the final product of a cracker baking process, but simplified the baking process to achieve this (Kweon, Slade, & Levine, 2011b). In order to better understand the complex interactions inherent in baking, and their effects on the baked product, as they occur in industry, it is necessary to study

baking in situ. This approach provides a process map, in which the development of product attributes is overlaid with processing conditions, and considered within the context of a timeline. Aspects of this approach were presented in Chapter 3, using an industrial cookie baking process. The current study expands on that work by presenting oven parameters (temperature, humidity, air velocity and heat flux data) from an industrial cracker baking process, and matching it with product data (internal temperature, moisture content, mechanical texture, and X-ray microtomography) to map product transformations.

Snack crackers are produced using a comparatively short (~3 minute) baking process, in which leavening, structural development and set, development of colour, and drying all occur. Crackers differ from cookies by being higher in moisture, and lower in sugar and fat. Both the formulations and baking processes used for crackers contribute to their characteristic flaky and open structure that distinguishes them from cookies. These characteristics were measured in cookies in the previous chapter, and the current study was developed to extend understanding of transformations in low-moisture dough products, and the baking processes that produce them, via the following objectives. First, this research investigated product transformations in low-moisture dough, and related these to aspects of the cracker baking process according to a timeline. Second, industrial oven profile data were emulated at the benchtop level.

4.2 Materials & Methods

4.2.1 Cracker Oven Profile

Access was obtained to an industrial baking facility, located in Montreal, and operated by Kraft Canada, Inc. A single baking line at the facility (line 3), that was used to produce Ritz Crackers, was evaluated. A profile of the oven was obtained with the use of a Scorpion[®] data logging measurement system (Reading Thermal Systems, Reading, PA, USA). Sensor arrays attached to the data logger were passed through the oven with the dough pieces. The frequency of sampling by the data logger was 0.5 seconds. Data from the logger was transferred to a computer for analysis after each run. All measurements were taken as close as possible to the middle of a timed production run to ensure that oven conditions had reached a steady state. Attributes of temperature, airflow, humidity and heat transfer were collected.

Temperature (Oven and Cracker)

Oven temperature data was collected using a Scorpion[®] Type B Air/Air temperature array. The sensor array consisted of 10, equally-spaced type-T thermocouples on an arm that spanned the width of the oven band. Thermocouples had an operating temperature range of -50 to 350°C, an accuracy of 1°C and a response time of 0.8 s in air at 1 m/s. A shield on the array between the thermocouples and the oven band minimized the influence of hot air coming through the band on temperature readings. Thermocouples were positioned at a height of approximately 5 cm above the oven band.

The Scorpion[®] apparatus was adapted to collect internal temperature data from dough pieces as they transited the oven. For this, a thin type-T thermocouple was inserted horizontally into a dough piece that was then attached to a modified humidity data logger via a product probe interface (PPI).

Total Heat

Convective and radiant heat fluxes were measured at product level using a Scorpion[®] heat flux sensor attachment. The sensor attachment had a black sensor that measured radiative and convective heat flux, and a gold-covered sensor that measured only convective heat flux. Sensor elements were type-T thermocouples with an operating temperature range of -50 to 350°C, an accuracy of $\pm 5\%$ of full scale and a response time of 3 s in air at 1 m/s.

Air Velocity

Air velocity was assessed using a Scorpion[®] air velocity sensor bar consisting of 10 equally spaced miniature hot-wire anemometers with type-T thermocouples on an arm that spanned the width of the oven band. Anemometers had a range of 0 to 8 m/s, a resolution of $\sim 2\%$ of air velocity, accuracy of $\pm 5\%$ of full scale and a response time of 3 s in air at 1 m/s.

Humidity

The absolute humidity of the baking process was assessed using a Scorpion[®] humidity sensor equipped with capacitive humidity chips and type-T thermocouples. Humidity

was determined using a high temperature moisture sensor, a low temperature moisture sensor and a bulk air (dry bulb) temperature sensor. The sensor had an operating temperature range of -50 to 350°C, an accuracy of $\pm 5\%$ of full scale, and a response time of 3 s in air at 1 m/s. Humidity was reported as kg water/kg dry air.

4.2.2 Cracker Dough Baking

The cracker dough used in this study was a proprietary commercial formulation with the following ingredient declaration: enriched wheat flour, vegetable oil shortening, sugar, salt, glucose-fructose, malt flour, sodium bicarbonate, ammonium bicarbonate, monocalcium phosphate, soya lecithin, soyabean oil with TBHQ and citric acid, amylase, protease, papain, yeast and sour dough culture. Sugar, water and fat content in the formulation were 7%, 22% and 8% (d.b.), respectively.

Cracker Dough Sampling Procedure

Samples were obtained from seven points throughout the process: from the conveyor at the oven entrance, via five ports in the side of the oven (oven Sampling Points 1 to 5, respectively), and at the oven exit. Details on the distance from the entrance and baking duration at each sampling point are shown in Table 4.1.

All samples were obtained from the right hand side of the oven. One set of samples was immediately submerged in liquid nitrogen to arrest further physicochemical changes.

These were then packed into plastic freezer bags and stored at -20°C for further analyses. A second set was taken to an on-site laboratory where moisture content and texture analyses were conducted after 30 minutes.

Table 4.1 Cracker process summary

Sampling Point	Oven Zone	Distance from Entrance (m)	Baking Duration (s)
Entrance	-	0	0
1	2	23.8	54.3
2	4	39.6	90.5
3	5	51.8	118.4
4	6	64.0	146.3
5	7	76.2	174.1
Exit	-	85.3	195

Moisture Content

The moisture content of dough pieces was assessed using an Ohaus MB45 moisture balance (Ohaus Corporation, Parsippany, NJ, USA). A 1-g sample was ground by mortar and pestle into the moisture balance pan and the balance was programmed to run at 130°C for 3 minutes.

Texture Analysis

Instrumental assessments of cracker dough texture were conducted with a TA.XTplus Texture Analyzer (Texture Technologies Corp, Scarsdale, NY, USA). The rig for compression testing was a 6-mm cylinder probe, and test settings were pre-test speed at 2 mm/s, test speed at 1 mm/s and distance at 1.3 mm. For the bend force test, a 3-point bend rig was utilized, and testing was carried out on cracker dough pieces from oven sampling point 2 onwards, as earlier samples were too soft to measure. Three-

point bend test settings were: distance between the supports was 25 mm, pre-test speed at 3.0 mm/s, test speed at 3.0 mm/s, and distance at 5 mm. For both compression and 3-point bend tests, a 5-kg load cell was used and maximum force, based on the average of three replicates, was reported.

4.2.3 Baking Cracker Dough in a Benchtop Oven

A benchtop Prototype Toaster Oven, hereafter PT oven (Figure 4.1) (ONIRIS, France) consisting of an insulated baking chamber with radiators positioned above and below a baking platform, was assessed for its ability to emulate the industrial cracker baking process. Radiators were ceramic infra-red emitters each rated at 500 W (Acim Jouanin, Nétreville, France). A type-T thermocouple inside the baking chamber reported air temperatures close to the surface of the baking crackers, while a thin, type-T thermocouple inserted into the cracker dough pieces reported their internal temperature. Heat supplied by the radiators was regulated externally and was programmable by computer.



Figure 4.1 Prototype toaster oven, ONIRIS, France

Model Cracker Dough

A model cracker dough formulation, developed for benchtop oven evaluation of flour quality by Kweon et al., (2011a) was used for the PT oven baking trial. The ingredients and formulation are provided in Table 4.2. Sugar, water and fat content in the formulation were 6.0%, 23.0% and 8.0% (d.b.) respectively. The flour was “Francine” brand, Type 45, containing 8.8% protein.

Table 4.2 Model cracker dough formulation

Ingredient	Quantity (g)
Flour	100 (13% moisture)
Sucrose	9
Salt	0.75
Sodium Bicarbonate	1.25
Ammonium Bicarbonate	1.25
Monocalcium Phosphate	1.25
Shortening	12.0
Water	29.0

Model Cracker Manufacture

Sodium chloride, monocalcium phosphate, sodium bicarbonate and flour were weighed into a container and thoroughly mixed. Sucrose was dissolved in warm water. The flour mixture was then placed into an alveograph (Chopin, Villeneuve-la-Garenne, France) along with the shortening. The ammonium bicarbonate was stirred into the sucrose/water solution. The alveograph was started and the sucrose/ammonium bicarbonate/water mixture was added to the dry ingredients for kneading. Dough was kneaded in the alveograph for 7 minutes at 35°C. After every minute of kneading, the alveograph was stopped and the sides were scraped down to ensure even distribution of the ingredients. The dough was removed to a sheeter where it was sheeted five times, to a thickness of approximately 2 mm. Dough was then cut using an oval hand-cutter (5.7 x 4.2 cm, with seven docker pins).

Model Cracker Dough Baking Procedure

Model cracker dough was baked in the PT oven following two procedures. The first followed the method of Kweon et al., (2011a), i.e. the PT oven temperature was set to 260°C, and baking proceeded for 150 s. The second procedure used lower temperature set points (160, 170 and 180°C) and a 195 s baking time as per the industrial oven process.

Internal dough piece temperature was recorded via a thin, type-T thermocouple inserted horizontally into the dough. Temperatures were logged using an attached computer.

4.2.4 Comparing Cracker Internal Structure

X-Ray Microtomography

Two microtomography systems were used to evaluate cracker structure. First, microstructure of fully baked crackers from the industrial process and of model crackers from the benchtop process were analysed by X-ray microtomography using a SkyScan 1174 X-ray microtomograph (Bruker-MicroCT, Kontich, Belgium). A quarter of a cracker was fixed to the turntable of the microtomograph for each scan. Scan settings were: 897 images collected over a 108° rotation, using an electron acceleration of 50 kV, a current of 800 μ A and a scan resolution of 29.75 μ m.

Images were reconstructed in SkyScan's Data Viewer program. White areas represented high X-ray attenuation, i.e. cracker matrix, and black areas represented pores inside the crackers i.e. air spaces. A filter to remove white speckles of < 40 voxels was applied to remove image noise.

X-ray microtomography also was carried out on industrially-baked crackers taken from each designated oven sampling point, from the oven entrance through to the oven exit. A Locus 130 in vivo X-ray microtomograph (GE Healthcare, London, ON, Canada) was used. Whole cracker dough pieces were stacked in a styrofoam sample cup and packed with foam to prevent movement during the scan. The sample cup was then taped to the sample gantry of the microtomograph. Scan settings were: 720 images collected over a 360° rotation, using an electron acceleration of 50 kV, a current of 450 μ A and a scan resolution of 47 μ m.

Images were reconstructed using Microview (GE Healthcare, London, ON, Canada). Scan data were corrected and microtomography values were calibrated using calibration phantoms. Calibration phantoms were a piece of unbaked cracker dough and an empty airspace. Following calibration, full resolution reconstruction of the crackers was performed by applying user defined 3-D Regions of Interest (ROIs).

4.2.5 Data Analysis

All data collected for industrial scale and model crackers were subject to analysis of variance (ANOVA). Where data sets were of variable size, Proc GLM was used to account for the variation. Significant differences between treatments were established using Tukey's HSD (Honestly Significant Difference) with significance set at $p < 0.05$. All analysis was conducted using SAS 9.2 (SAS Institute Inc., Cary, NC, USA).

4.3 Results

4.3.1 Industrial Baking

As cracker dough samples were collected from access points on the right hand side of the oven, it was necessary to ensure that data collected using the Scorpion[®] reflected conditions in this location. While the Scorpion[®] sensor bar extended across the full width of the oven, only data from the four sensors on the right hand side were used for characterization. When shorter (single sensor) Scorpion[®] data acquisition attachments were used, they were placed on the right hand side of the oven band to ensure consistency in the location of data collection.

Oven and Cracker Temperatures

Oven air temperature increased rapidly at the beginning of the process and eventually reached a maximum of 234°C towards the end of baking (Figure 4.2). The temperature of the oven band rose rapidly to approximately 70°C in the first 6 seconds of baking then increased steadily to 183°C thereafter. The internal temperature of cracker dough pieces increased steadily throughout baking from 39°C to 156°C.

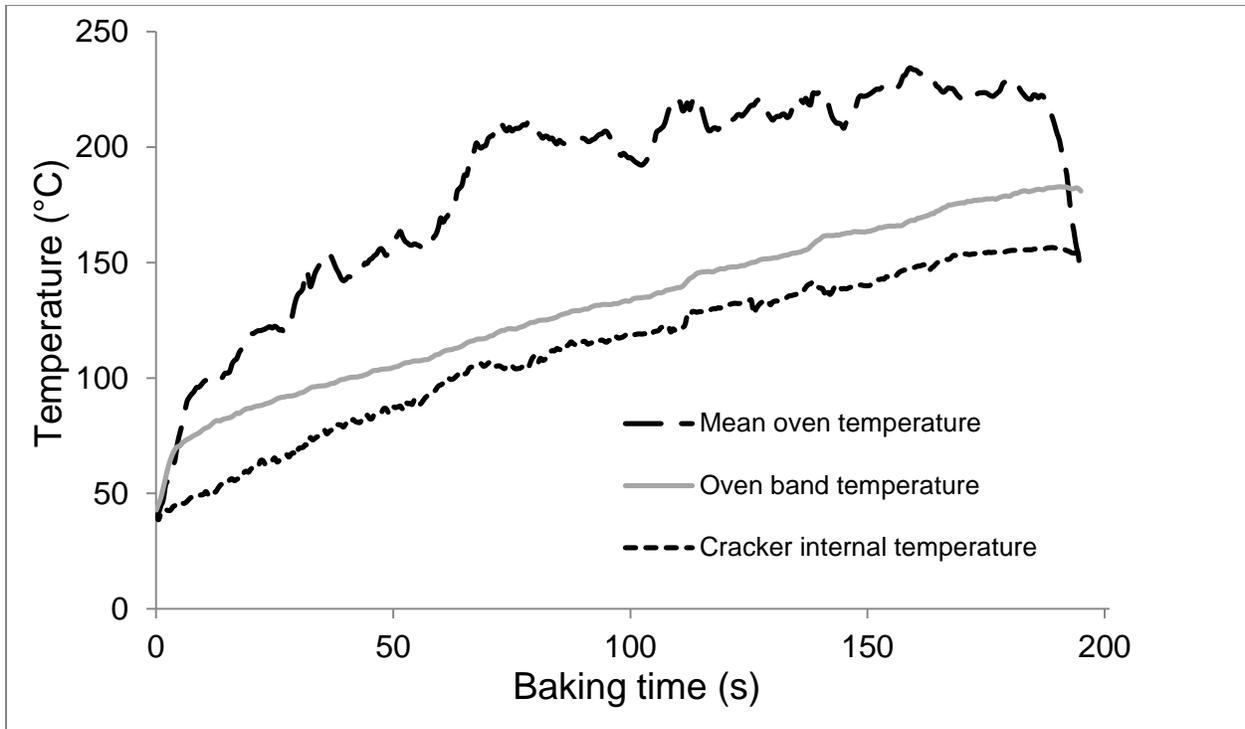


Figure 4.2 Oven and internal temperature profile of crackers during baking

Heat Flux and Air Velocity

Radiative heat flux increased steadily with a large peak occurring between 60 and 70 seconds (Figure 4.3). This peak, also seen in the mean oven (air) temperature values of Figure 4.2, was related to a region of the oven in which air temperature also increased rapidly. In contrast, convective heat flux showed a series of regularly-spaced peaks throughout baking that corresponded to peaks in air velocity at matching points in the process (Figure 4.4). Mean heat flux in the process was 7100 W/m^2 . Cumulative values of heat flux were collated in order to determine a total heat value for the process of 1.399 GJ/m^2 , with 33% of this being radiant and 67% being convective (Figure 4.5).

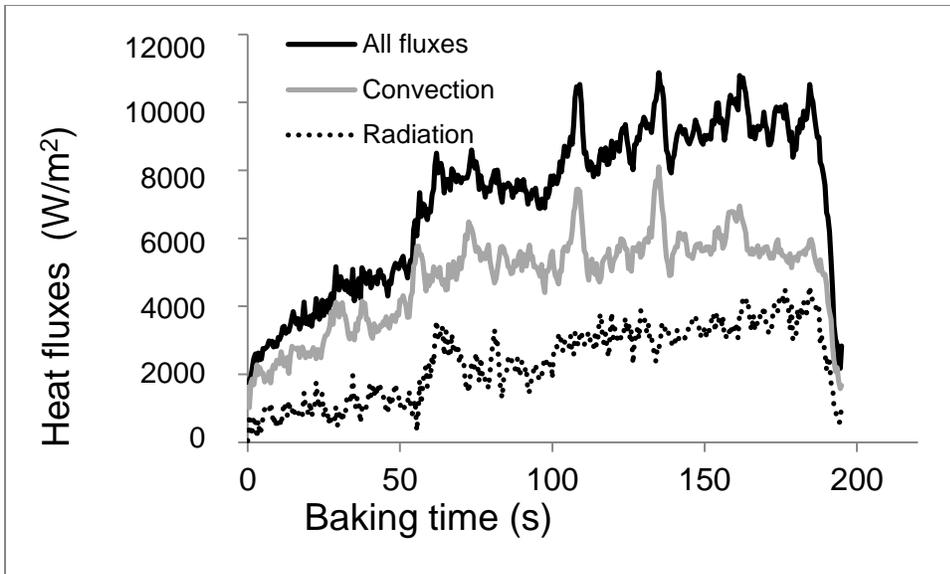


Figure 4.3 Heat transfer received by crackers

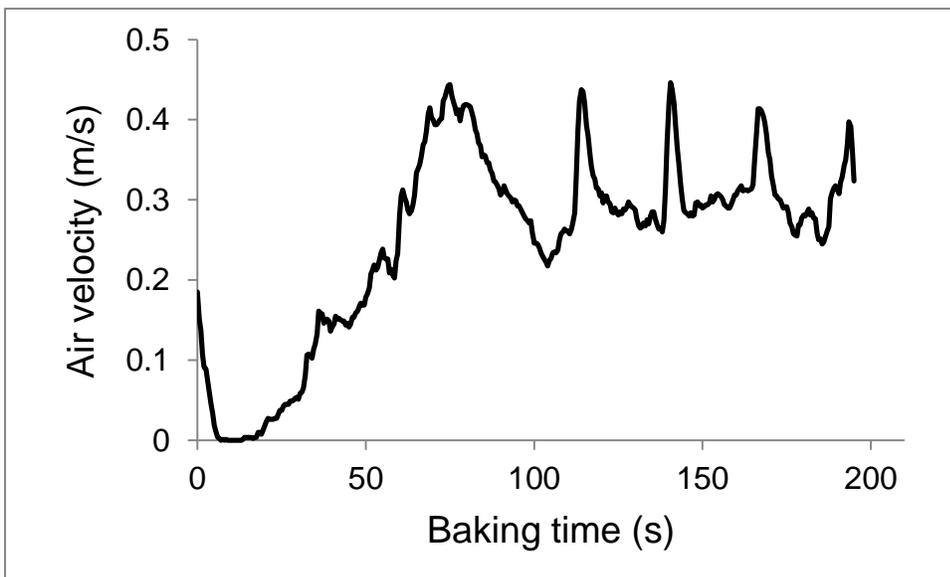


Figure 4.4 Air velocity in tunnel oven during cracker baking process

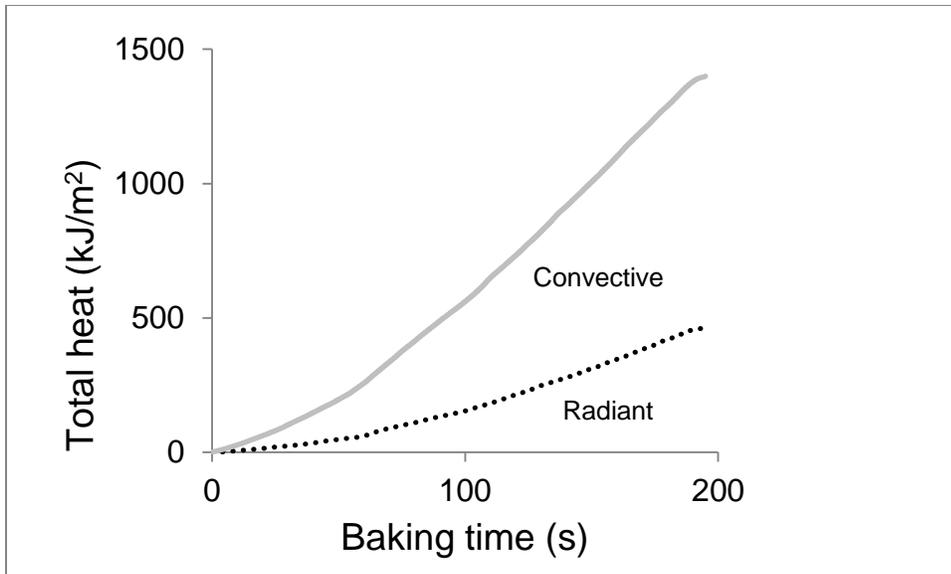


Figure 4.5 Total heat of tunnel oven during cracker baking process

Humidity and Moisture

Absolute humidity of the air in the oven increased as baking progressed and peaked at 0.35 kg H₂O/kg dry air, after which it declined (Figure 4.6). Moisture content of the dough decreased constantly throughout baking with the exception of a temporary slowing between sampling points 2 and 3, and after sampling point 5 (Figure 4.7). To evaluate the amount of water being removed to the oven atmosphere between each sampling point, dough piece weight loss values were factored into an equation including the total number of dough pieces known to transit the oven within the 195 s baking time. This made it possible to calculate the mean rate of water removal per second within each region, where a region refers to an area between two sampling points (Figure 4.8). For this calculation, the assumption was made that 100% of the weight loss from the dough was water. Examination of the water removal rate by region highlighted that the majority of water was removed from the dough pieces at the beginning of baking.

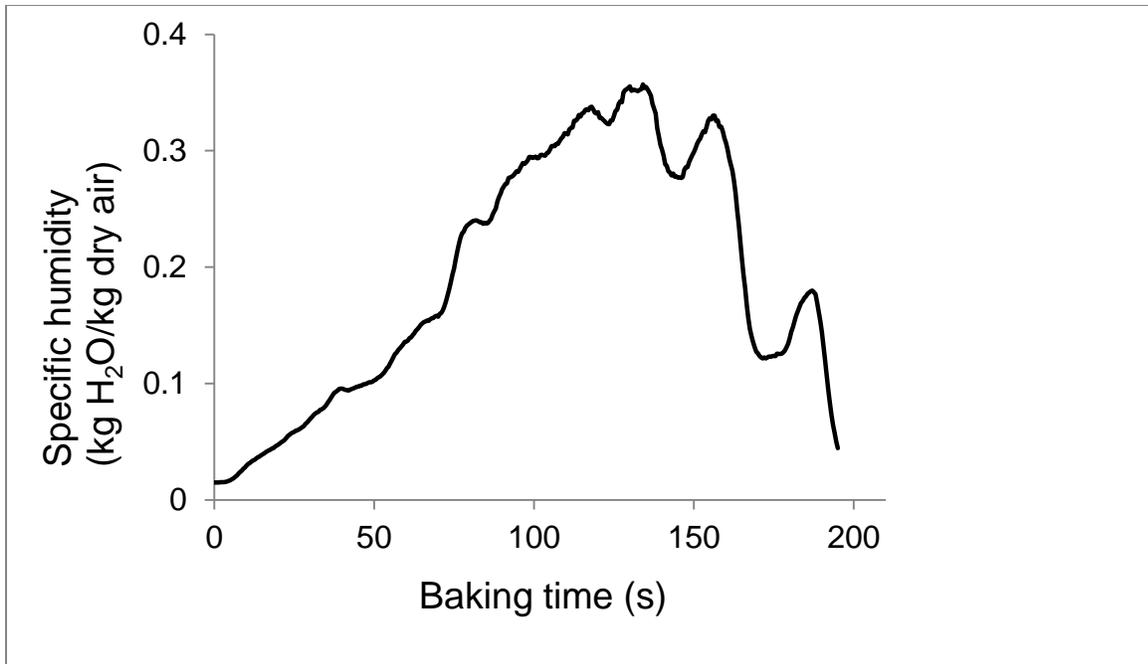


Figure 4.6 Specific humidity of air in tunnel oven during cracker baking process

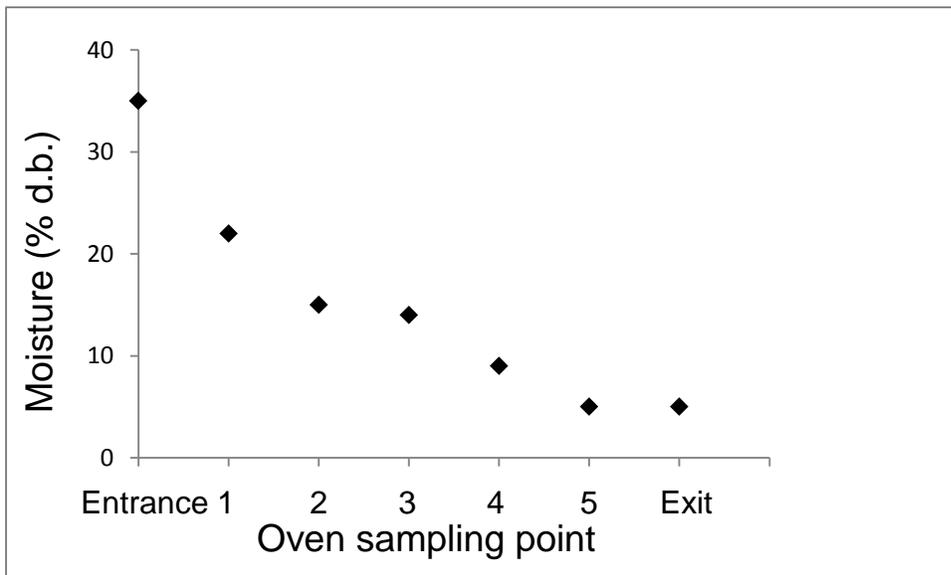


Figure 4.7 Moisture content of cracker dough pieces during baking

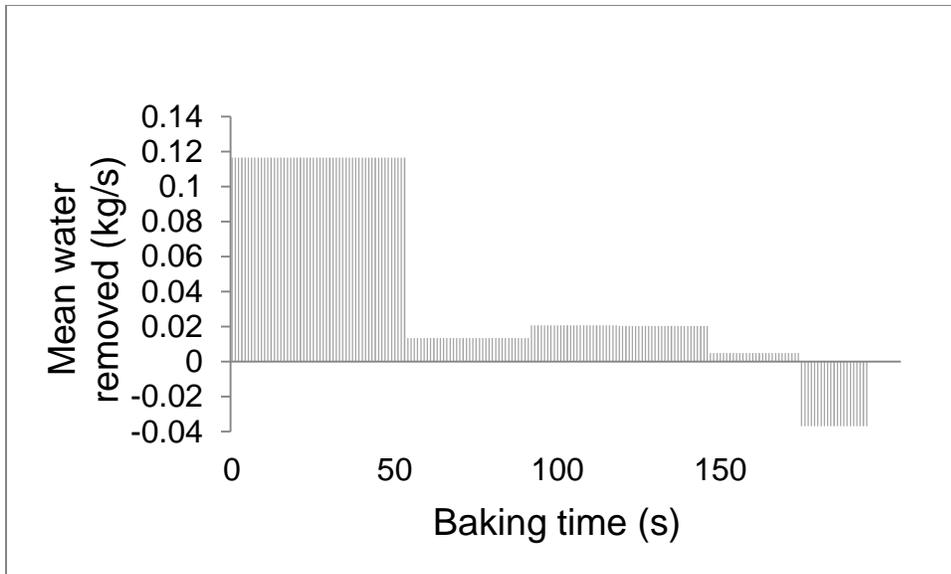


Figure 4.8 Mean weight of water transported per second from dough pieces to oven atmosphere during baking

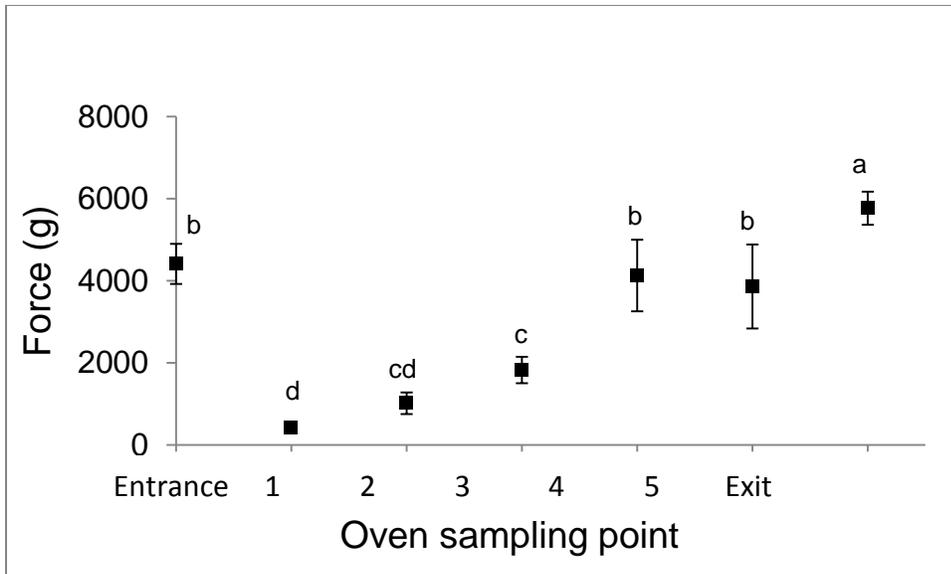
4.3.2 Cracker Dough Texture

Compression

The force required to compress the cracker dough pieces decreased significantly from the entrance to the first in-oven sampling point (Figure 4.9). However, from the first in-oven sampling point onwards there was then a steady and significant increase seen in force to compress the cracker dough through to the end of baking.

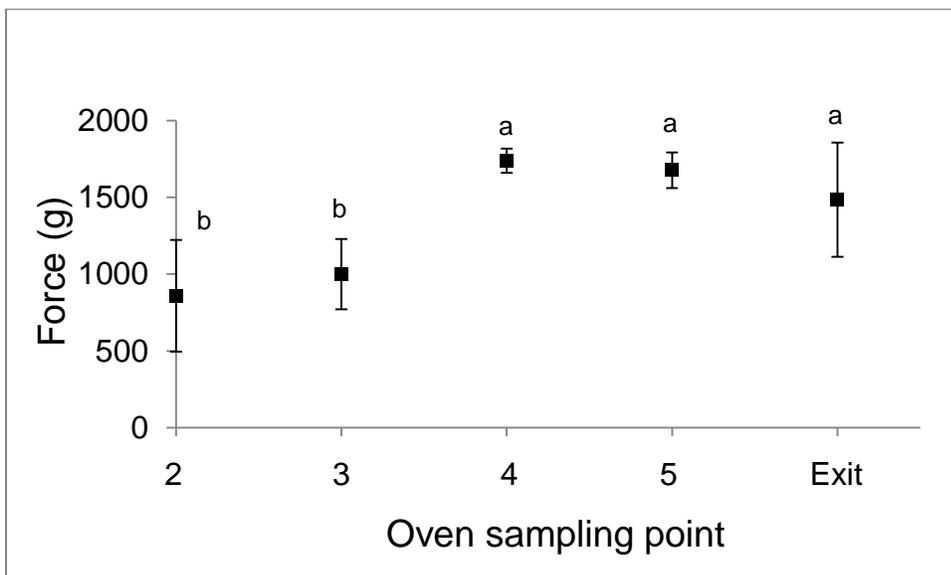
Three Point Bend

The force required to snap the cracker dough pieces increased significantly between in-oven sampling points 3 and 4, and remained at this level through to the end of the baking process (Figure 4.10).



Sampling points with the same letter were not significantly different ($p < 0.05$)

Figure 4.9 Force to compress crackers sampled from industrial baking oven



Sampling points with the same letter were not significantly different ($p < 0.05$)

Figure 4.10 Force to snap crackers sampled from industrial baking oven in 3-point bend test

4.3.3 Benchtop Cracker Baking

Model cracker dough baked in the PT oven at a set temperature of 260°C, as per Kweon et al., (2011a), was found to blister rapidly and burn, as shown in Appendix A. Crackers baked using the lower initial set temperatures of 160, 170 and 180°C were found to leaven and bake without burning. Air temperatures above the model cracker dough in the PT oven are shown against air temperature in the industrial oven (Figure 4.11a). Model dough internal temperatures in the PT oven are shown against dough internal temperature from the industrial oven (Figure 4.11b).

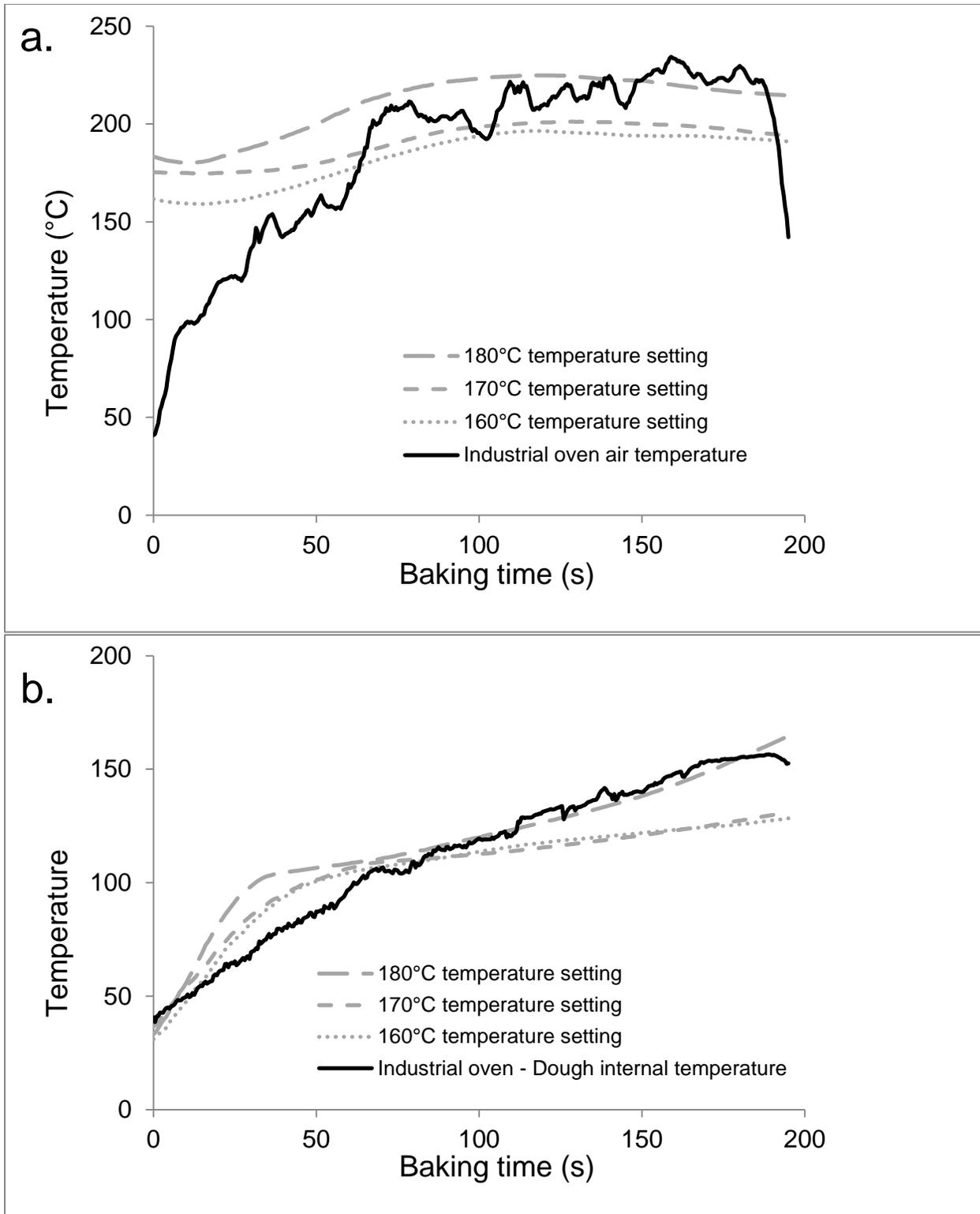


Figure 4.11 Air temperatures (a) and dough internal temperatures (b) from PT oven compared to temperatures obtained in industrial tunnel oven

Manipulation of the PT Oven, by providing feedback from the internal temperature probe to switch the radiators off and on, allowed crackers to be baked to similar internal temperature profiles to those of the industrial process. Using this approach, crackers were produced with the appearance (i.e. leavened, browned, not burnt) of industrially baked crackers with a matching moisture content. A comparison of mean internal cracker temperature (n=10) of crackers baked in the PT Oven using this method versus crackers from the industrial oven is shown in Figure 4.12.

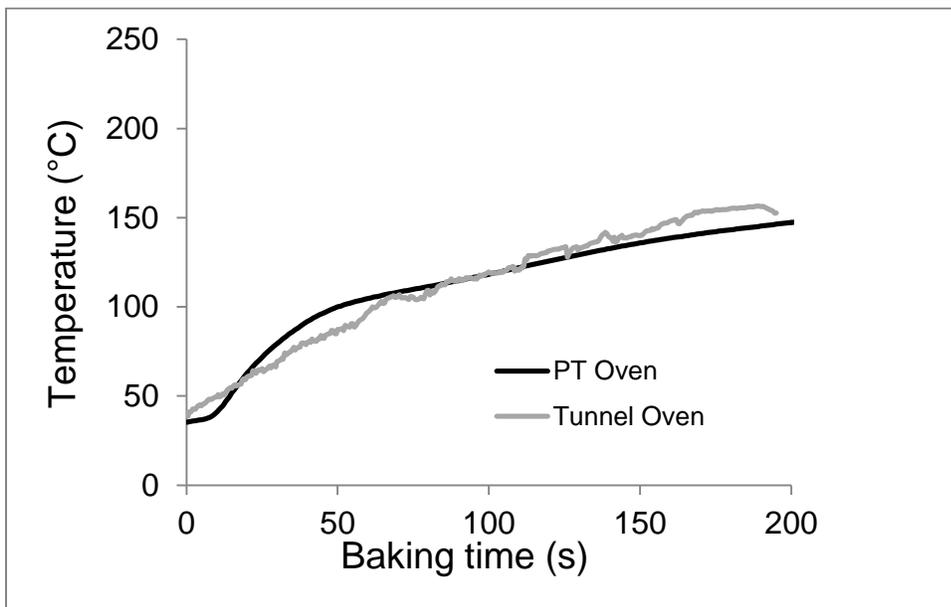


Figure 4.12 Mean internal temperature of crackers baked in industrial tunnel oven vs. crackers baked in PT Oven

4.3.4 Comparison of Cracker Internal Structures

X-Ray Microtomography: Industrial versus PT oven Crackers

A qualitative comparison of the X-ray microtomography slices showed that the industrially produced crackers had an open structure, characterized by a number of large and intermediate air cells, in addition to many smaller cells (Figure 4.13). The model crackers, baked in the PT oven, contrasted with the industrial crackers by having many small, and few intermediate, air cells.

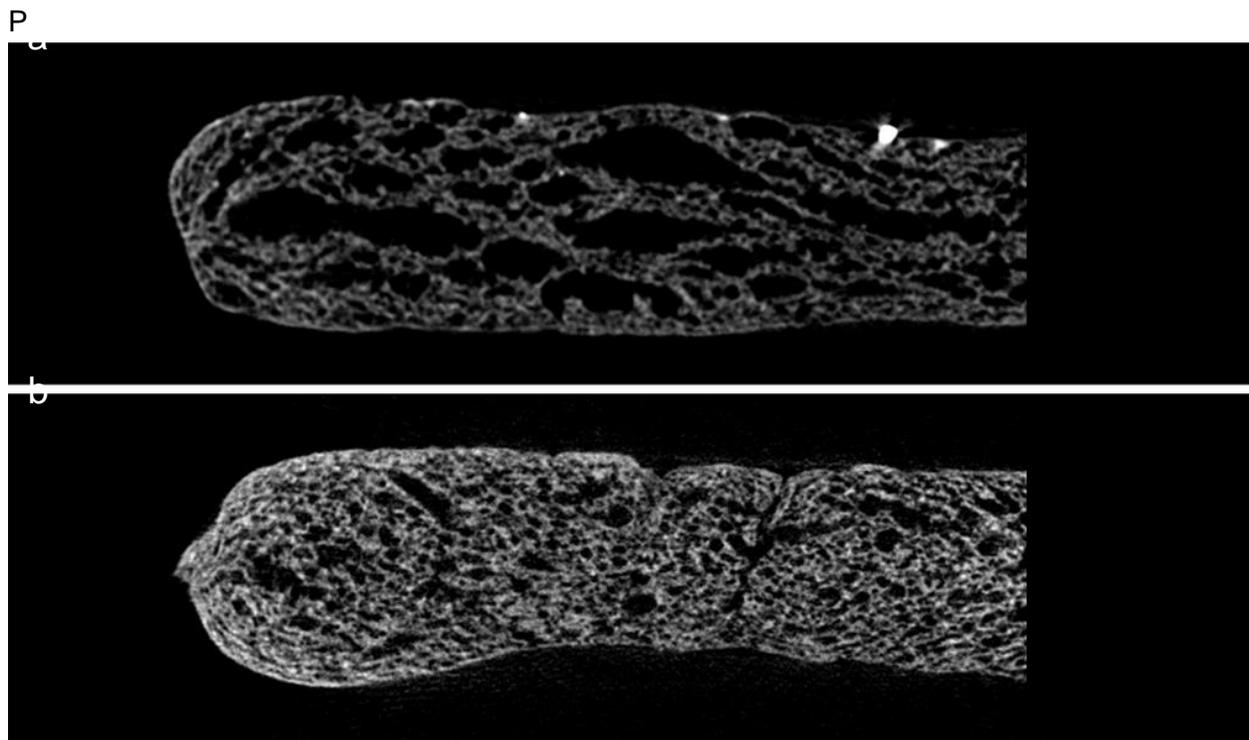
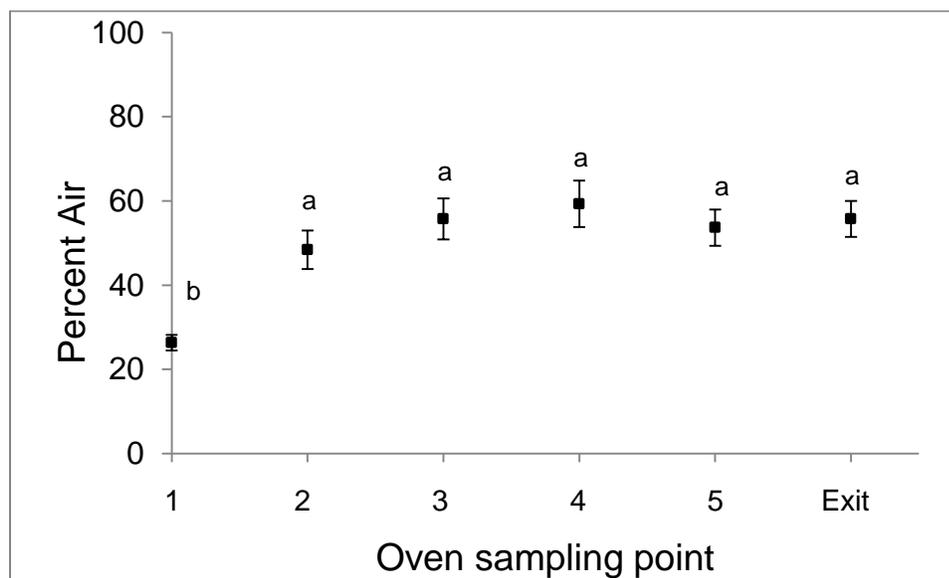


Figure 4.13 Images from a front slice (ZX axis) of an industrially produced cracker (a) and a model cracker (b)

X-Ray Microtomography: Industrial Crackers Throughout Baking

The cracker dough samples obtained from the oven entrance did not contain air cells that were quantifiable at the resolution used for this microtomography analysis.

Measurable air cells were apparent from sampling point 1 in the industrial oven onwards. Analysis of air cells as a percentage of the volume of the ROI's showed that the percentage of air in the crackers increased significantly from the first oven sampling point to the second, and remained at this higher level until the end of baking (Figure 4.14).



Sampling points with the same letter were not significantly different ($p < 0.05$)

Figure 4.14 Percent air cell volume of industrially baked cracker dough throughout baking

4.4 Discussion

4.4.1 Industrial Baking

The industrial cracker baking process was characterized by its high temperature and short duration. Air temperature just above the oven band was 100°C within 14 s, and 200°C within 68 s. This was similar to, but more rapid than, the rate of temperature increase in the cookie baking process (Chapter 3) where air temperature was 100°C

within 36 s and 200°C within 78 s. Internal cracker temperature also increased rapidly from 40°C to 100°C within 63 s, and achieved a maximum of 156°C by the end of baking (195 s). These high internal temperatures observed during baking can be attributed to the low-moisture content of the dough, and their comparatively high fat and sugar contents. Others also have observed this. For example biscuits baked at 250°C were shown to achieve internal temperatures of 210°C (Fahloul, Trystram, Duquenoy, & Barbotteau, 1994). A high moisture content precludes such high internal temperatures in other baked products; bread crumb, for example, reached a maximum of only 98 °C despite being baked in an oven at 200°C for 21 minutes (Le-Bail et al., 2011).

The mean heat flux value found in the industrial cracker baking process during baking was 0.71 W/cm², and the total heat of the process was 1,399.8 kJ/m² (Figure 4.5). For comparison, the total heat in the cookie baking process described in Chapter 3 was 2,215.6 kJ/m², although this was expected due to the cookie baking process being approximately twice the duration of the cracker baking process (406 s versus 195 s). Heat flux values of matching industrial baking processes are not available in the literature for comparison, although there are published values for laboratory and pilot processes with semi-sweet biscuit. A 15-m pilot oven, indirectly fired with multiple burners using natural gas, was found to provide peak heat flux values of approximately 0.25 W/cm² (Fahloul, Trystram, McFarlane, & Duquenoy, 1995). Similarly, a static pilot plant built to mimic baking conditions in continuous ovens, and electrically heated, was found to produce a range of heat flux values. Depending upon the location of the heat flux sensor, the set point temperature, and the velocity of air in the baking chamber, these values ranged from 0.17 - 0.62 W/cm² (Zareifard et al., 2006).

Heat flux in a baking process consists of radiative, convective and conductive heat flux modes (Incropera, DeWitt, Bergman, & Lavine, 2006). In the current study, however, measurement was limited to radiative and convective fluxes (Figure 4.3). Total heat in the cracker (and cookie) baking process will, therefore, be somewhat greater than the values indicated. An estimate of the relative contribution of the conductive heat flux component was given by Fahloul et al., (1995), who found conductive heat flux in a 15-m pilot oven to be 10-11% of total heat.

An interaction was observed between heat flux (Figure 4.3) and air velocity (Figure 4.4), with these figures showing matching peaks at corresponding baking times. The increases in convective heat flux shown in Figure 4.3 occurred when air velocity increased and were characteristic of extraction vent placement. This effect was documented in the process described by Fahloul et al., (1995) and also in multi-zone industrial ovens described by (Baik et al., 2000).

The absolute humidity peak of 0.35 kg H₂O/kg dry air was higher than the published values of 0.19 kg H₂O/kg dry air found in a similar gas fired tunnel oven in which cakes were baked (Baik et al., 2000). However, differences between ovens and the products being baked make such comparisons difficult. In the current study, as baking progressed, the absolute humidity within the oven increased, as the air had nowhere to go until it was removed from the oven (via extraction vents and the oven exit). Although much of the moisture reported as absolute humidity represented water being baked out of the dough, the absolute humidity values obtained here cannot be quantitatively related back to the crackers due to the removal of air, and thus moisture from the oven

during baking. Additionally, there will be a contribution to absolute humidity from oven combustion products (Baik et al., 2000).

Evaluation of the moisture content of the dough pieces at each sampling point confirmed a loss of moisture from the product throughout baking that would be responsible for influencing humidity. The change in dough piece moisture (Figure 4.7) was constant throughout baking with the exception of a temporary slowing after 90.5 s and apparent reversal after 167.1 s. The small increase in moisture content of the final samples was unexpected, but was validated by the cracker weight which also increased at this point (Appendix A). This weight and moisture gain during the final stage of baking may be attributed to the very dry cracker pieces rapidly absorbing moisture from the air upon exit to the moist bakery atmosphere before these samples could be weighed.

Unlike the oven humidity data and cracker moisture data, which suggested approximately constant water removal to the oven atmosphere, the cracker weight data suggested that the majority of water was removed at the beginning of baking, specifically between the entrance and the first sampling point.

4.4.2 Cracker Dough Texture

Compression

The observed decrease in force to compress cracker dough that occurred between the oven entrance and the first sampling point in the oven coincided with the rapid warming of the dough (Figure 4.2) and the beginning of leavening (Figure 4.14). These effects, warming, which caused fats and gluten to soften, and leavening, leading to increased

air space and decreased density in the dough, were typical of changes in dough that occur early in baking (Manley, 2000).

Compression testing beyond the first in-oven sampling point showed a steady increase in firmness thereafter (Figure 4.9). While the dough contained a significantly greater proportion of air by the second in-oven sampling point, there was no corresponding significant difference in compression force. This would be due to the decreased density of the dough, which would decrease the required compression force, being countered by other thermally triggered changes in dough structure, e.g. gluten coagulation and starch gelatinization (Manley, 2000). The setting of cracker structure as baking progressed resulted in further increases in compression force, and this corresponded with a continued loss of moisture. That is, cracker structure became harder, and thus required more force to compress, as it was dried. The force to compress Ritz crackers has been shown to decrease as a_w increased (Kohyama, Nishi, & Suzuki, 1997), a finding that indirectly supports the finding that water removal from crackers increases hardness.

Three Point Bend

The results of the 3-point bend test also reflected the development of cracker structure seen in compression testing. It is hypothesized that the observed significant increase in force that occurred between oven sampling points 3 and 4 was the result of moisture removal and setting of product structure, notably gluten thermal set. Gluten thermal set occurs in bread when the gluten matrix, developed during mixing, is reinforced by protein aggregation during the baking process (Chevallier, Colonna, Buleon, et al.,

2000). Similar to bread, the dough used in the current study was kneaded prior to baking, thereby allowing possible gluten strand development, and protein aggregation to occur. While the structure of the crackers continued to increase in firmness, as shown by the compression test, the failure of 3-point bend force to increase over the final 3 sampling points is likely due to the crackers becoming more brittle as their structure sets, thus requiring no further force to break from sampling point 4 onwards. This explanation is supported by 3-point bend data from crackers demonstrating that fracture strength was not dependent on moisture content (Kim & Okos, 1999).

4.4.3 Benchtop Cracker Baking

The ability to manufacture a model, chemically-leavened cracker in the lab, that had characteristics similar to an industrially-baked cracker, has been demonstrated (Kweon et al., 2011a, 2011b). However, this method required baking at 260°C for 5-6 minutes, depending upon dough weight, in a static single-chamber oven. While the final product attributes may have been similar to that of an industrially produced cracker, only the product, and not the process, was emulated.

One objective of the current study was to bake crackers on the lab benchtop, using parameters obtained from an industrial process, i.e. to emulate the process and the product. The cracker baking process profiled in the current study used a complex profile that included a short (195 s) baking time, and a set of conditions that rapidly raised the internal temperature of the dough piece, in order to move water out of the dough early in baking (Figures 4.7 and 4.8). While the PT oven was not built to allow manipulation of air velocity and humidity, it was possible to bake model crackers within other constraints

of the industrial process. These were baking time and internal product temperature. As shown in Figure 4.12, the similarity in the time/internal temperature curves of the industrially-produced cracker and the PT oven cracker suggested that this initial level of process emulation was achieved. However, the PT oven was effectively a 100% radiant heating device, and the industrial oven was found to supply 33% radiant and 67% convective heat (Figure 4.5). It was necessary to alter PT oven temperature settings for the process to produce crackers that achieved sufficient browning and leavening, without being burned. A 180°C temperature set point in the PT oven, that gave similar internal product temperatures to the industrial process, did not produce in-oven air temperatures matching those of industrial baking (Figure 4.11). These findings can be explained by differences in heat transfer modes between each baking process. That is, at equivalent temperature settings, a mostly radiant baking process will lead to significantly more browning than a mostly convective baking process. This was shown in a cookie baking process in which higher cookie surface temperatures resulted from radiant heating versus convective heating despite air temperature being the same (Shibukawa, Sugiyama, & Yano, 1989).

X-ray microtomography examination of fully baked crackers from each process highlighted a further (unquantified) difference between baking outcomes, in which PT oven baked crackers appeared to have a different internal cellular structure than industrial crackers (Figure 4.13). The presence of many small, and few large cells in PT oven baked crackers, was suggested as being the result of different baking conditions. While the internal temperature profiles of the crackers were similar, they were not exactly matched, and Figure 4.12 shows an apparent faster initial temperature increase

in PT oven crackers. This temperature increase, combined with a likely lower humidity value, due to the open baking chamber of the PT oven, could facilitate faster thermal set of cracker structure, thereby inhibiting cell expansion. X-ray microtomography conducted on the industrially-baked crackers found there was no significant difference in air cell volume as a percentage of cracker total from the second in-oven sampling point onwards (Figure 4.14). This suggests that cracker leavening occurred only in the early part of the baking process, and was completed by the second in-oven sampling point. This was the same region in which the more rapid temperature increase occurred in the PT oven baked crackers.

4.5 Conclusions

While baking crackers on a lab-based scale using the PT oven would clearly not be suitable for full emulation of an industrial tunnel oven, this method was shown to bake crackers to similar internal temperature parameters over a set time. Successful emulation of starch transformations in the context of low-moisture baked goods requires the ability to bake model products in the lab to known moisture levels, over specific times and at controlled temperatures such that the starch component would be subject to appropriate time/temperature/moisture conditions. From this perspective, the use of the PT oven, when informed by process profiling data such as that from a Scorpion[®], may prove valuable to the ability to generate model products without having to resort to expensive and productivity interrupting production scale runs on industrial bakery equipment.

Chapter 5 The Evolution of Starch Transformation During Baking of Crackers

5.1 Introduction

The initial moisture content of dough is important to the component interactions and product attributes of baked goods. Bread dough, for example, has a higher moisture content (~70% d.b.) compared to cracker dough (~35% d.b.). This difference will result in different extents of transformation in starch and will impact other component interactions that transform the dough into products with specific desired attributes. The transformations of starch and other interactions in a bread-type system are fairly well understood (Goesaert et al., 2005). However, when dough systems contain lower levels of moisture, the interactions and behaviour of components such as starch are altered. Furthermore, low-moisture dough products also typically differ from higher moisture dough products in that they are baked to a moisture content of < 5% d.b. (Manley, 2000). These low-moisture baked products are extremely diverse in their composition, but largely can be grouped as either cookies or crackers. Cookies are distinguished by being short dough products with very low initial dough moisture contents, often less than 20% (d.b.). In cookies, plasticity is conferred by sugar and fat, and the cohesiveness of such short dough has been determined to be unrelated to any action of proteins such as gluten (Chevallier, Colonna, Buleon, et al., 2000). Crackers on the other hand contain a greater proportion of water, less sugar and less fat. This additional available water may enable the gelatinization of some starch within crackers during baking. Further, the flour

used in cracker production is also typically higher in protein (9-10%) than that used for cookies (7-8%) (Osella et al., 2008). This greater amount of protein results in the development of a gluten-based matrix. These differences in composition contribute to distinctly different textural attributes between cookies and crackers, and the role of starch in each, and the amount and availability of moisture to take part in interactions, are key to the development of structure during baking. The effects of starch-water interactions on cookie structure (Donelson & Gaines, 1998) and the nature of starch transformations in cookies have been described (Chevallier et al., 2002). Less research, however, exists examining these effects in cracker-type products.

In order to quantify changes to starch during baking, starch can be isolated to assess its pasting and thermal properties, as well as its crystallinity. The use of methods to assess these properties is common in starch research (Buléon, Véronèse, & C, 2007; Kim & Walker, 1992; Mamat et al., 2010). The effects of thermal processing on starch in low-moisture dough have been investigated previously in extrusion cooking of 40% d.b. pasta dough made from rice flour (Marti, Pagani, & Seetharaman, 2011). However, there is little literature available examining wheat starch that has been baked in the context of low-moisture products and then isolated for analysis of transformations. This may be due in part to findings in earlier research, such as that on cookies, demonstrating the role of starch as filler. In these systems, the starch granules remain virtually unchanged and simply become “embedded in a matrix of aggregated protein, lipids and sugars” (Chevallier, Colonna, Buleon, et al., 2000). As crackers contain a greater proportion of water than cookies, and considerably less than in cakes or breads, it is hypothesized that starch transformation in crackers would be intermediate in nature,

i.e. the initial stages of gelatinization, such as granule swelling, may be observed alongside limited leaching of amylose. It was also anticipated that the relatively greater moisture content of crackers would allow for detection of changes to starch thermal properties as differential scanning calorimetry (DSC) has been shown to detect thermal transitions in systems with moisture contents as low as 40% (d.b.) (Goldstein, Nantanga, & Seetharaman, 2010). Although many of the processes that impact starch during baking are well understood, there is little research available that maps starch transformation in low-moisture dough products during the baking process. Therefore, the objective of this study was to characterize the transformations that occurred in starch in snack crackers baked in an industrial oven.

5.2 Materials & Methods

5.2.1 Sample preparation

The cracker dough used in this study was of the same formulation as described in Chapter 4.

5.2.2 Cracker Dough Sampling Procedure

The procedure used to sample cracker dough from the oven was the same as described in Chapter 4.

5.2.3 Starch Isolation

Starch was isolated from dough samples using a protease-based extraction method adapted from Marti et al., (2011), and described in Chapter 3. For this method, ground samples were suspended in protein extraction buffer before being washed and incubated overnight with trypsin and papain. Samples were later washed in ethanol and dried with acetone before being ground by mortar and pestle for further analysis.

5.2.4 Moisture Content

Moisture content of dough was assessed using an Ohaus MB45 moisture balance (Ohaus Corporation, Parsippany, NJ, USA). A 1-g sample was ground into the moisture balance pan by mortar and pestle and the balance was programmed to run at 130°C for 3 minutes.

5.2.5 Microscopy

Bright-field and polarized light microscopic examinations to evaluate birefringence were conducted on starch extracted from dough and crackers from each sampling point through to the end of the baking process using an Olympus BX60 Microscope (Olympus Optical Co. Ltd., Japan) at 40x magnification. Images were captured using an attached Olympus DP71 camera. Granule sizes were assessed in ImageJ software (Wayne Rasband, National Institutes of Health, USA, version 1.46r) using a graphics tablet (Wacom CTL-471M) calibrated against a slide containing a known scale and photographed at the same magnification.

5.2.6 Thermal Properties

The thermal properties of the starch were assessed using a Differential Scanning Calorimeter (TA Q1000, TA Instruments, New Castle, DE, USA). Samples were weighed into alodined aluminum pans 1:3 (w/w) with DI water, sealed and left to equilibrate for 24 hours at room temperature. Heating proceeded at 5°C per minute from 25 to 120°C. An empty pan was used as a reference. Onset temperature (T_o , °C), peak temperature (T_p , °C), conclusion temperature (T_c , °C) and gelatinization enthalpy (ΔH , J/g) were determined using Universal Analysis 2000 software (TA Instruments, version 4.7A). All analyses were conducted in duplicate.

5.2.7 Crystallinity

Wide-angle X-Ray Powder Diffraction measurements were conducted on isolated starch samples (~0.1 g) from cracker dough (Entrance), partly baked crackers from Oven Sampling Point 1, and fully-baked crackers (Exit), using a Rigaku Powder Diffractometer (Rigaku Co., Tokyo, Japan). $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54 \text{ \AA}$) was selected using a quartz monochromator. The diffractometer settings were: current, 40mA; voltage, 40kV; scan speed, 1° per minute; range, 3-35° 2θ ; and sampling width, 0.02°. Data were smoothed using Jade 6.5 software and were normalized to equal total scattering in the 3-35° 2θ range. Peaks were fitted to the diffractograms and their position, area and width were assessed using Igor Pro software (WaveMetrics, Inc., version 6.0.5.0).

5.2.8 Pasting Properties

The pasting parameters of the starch isolates were assessed using a Rapid Visco Analyser (RVA-4™, Newport Scientific Pty. Ltd, Warriewood, NSW, Australia). The Standard 2 method was used, and data were analyzed in Thermocline for Windows (TCW3) software. Treatments were mixed with DI water in a RVA canister on an 8% dry weight basis to achieve 28 g total weight, and then allowed to hydrate for 1 hour prior to testing. Two pasting curves were collected for each treatment and the means of these replicates was reported.

5.2.9 Data Analysis

Data collected for each test were subject to analysis of variance (ANOVA). Significant differences among treatments were established using Tukey's HSD (Honestly Significant Difference) with significance set at $p < 0.05$. All analysis was conducted using SAS 9.2 (SAS Institute Inc., Cary, NC, USA).

5.3 Results

5.3.1 Moisture

Dough pieces were deposited onto the pre-warmed (returning) oven band at an ambient air temperature of approximately 35°C and did not lose any detectable quantity of moisture before entering the oven. Once in the oven, moisture loss was rapid in the early stages of baking, slowed between oven sampling points 2 and 3, increased again between sampling points 3 and 5, and remained constant through to the exit (Figure 5.1). This corresponded to the pattern seen for internal temperature of the dough pieces, wherein internal temperature increased rapidly from 35°C to 100°C initially and the rate of increase was slower from 100°C to 150°C, and then remained unchanged from oven sampling point 5 until the exit (Figure 5.1).

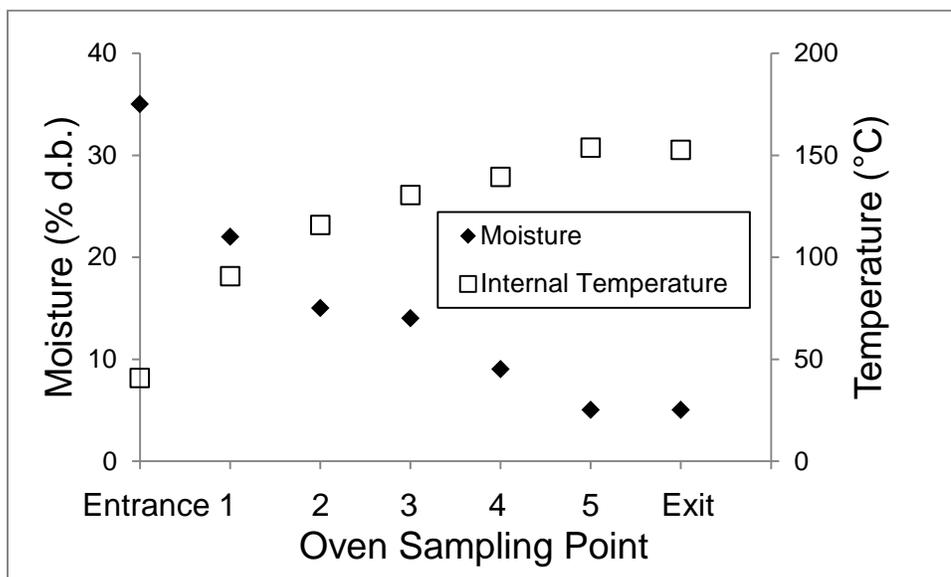


Figure 5.1 Change in moisture content of snack cracker dough during baking

5.3.2 Microscopy

Intact A- and B- starch granules that exhibited birefringence under polarized light were visible in starch samples extracted from unbaked cracker dough (Figure 5.2a, b) and from crackers from sampling point 1 (not shown). Loss of birefringence was observed from the oven sampling point 2 onwards, and swollen, non-birefringent A-granules were seen from this point through to the exit (Figure 5.2). Unlike the A-granules, the smaller B-granules remained birefringent throughout baking. Measurement of starch particle sizes in the micrographs showed different effects by population (Figure 5.3). The mean particle size of A-granules showed a statistically significant increase from ~20 μm prior to baking to ~30 μm at the end of baking, with the size increase occurring all at once between oven sampling points 1 and 2. In contrast, B-granules showed a small (1-2 μm), but statistically significant, shrinkage throughout baking. Although significant, the apparent change in size of the B-granules may have been a consequence of the measurement method used.

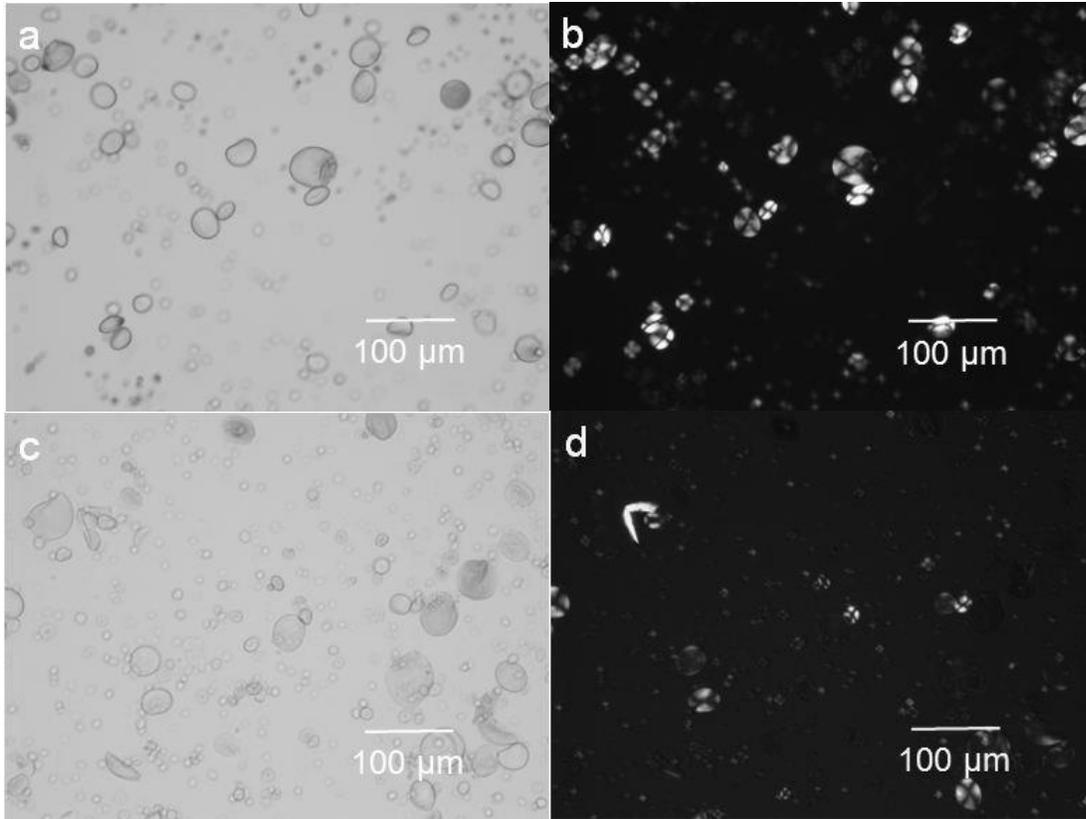


Figure 5.2 Selected light micrographs of starch extracted from cracker dough (Entrance) and fully baked (Exit) crackers (a and b = dough starch, bright field and crossed polarizers respectively, while c and d are cracker starch)

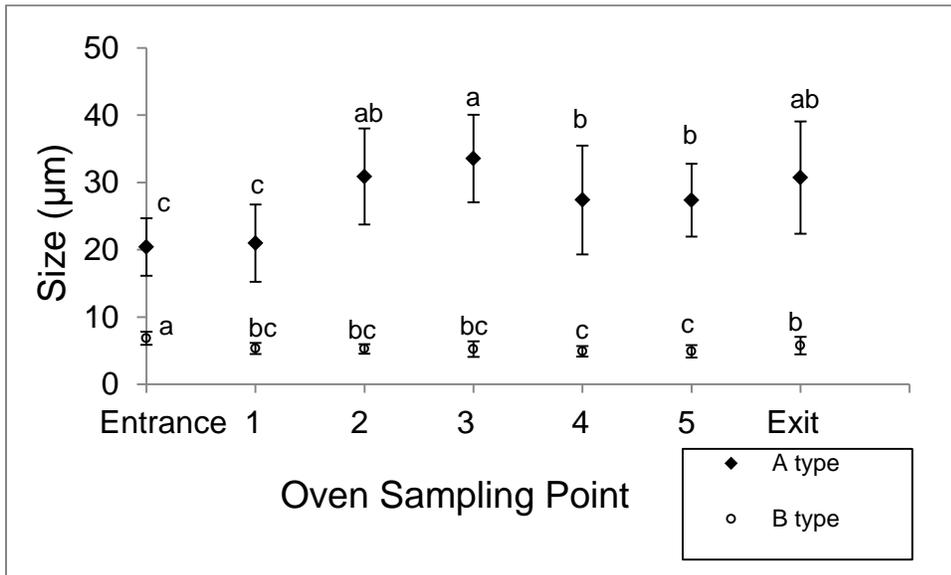


Figure 5.3 Mean size of A and B type starch granules in crackers throughout baking (Data points within each set (A-type or B-type) having the same letter are not significantly different at 95%)

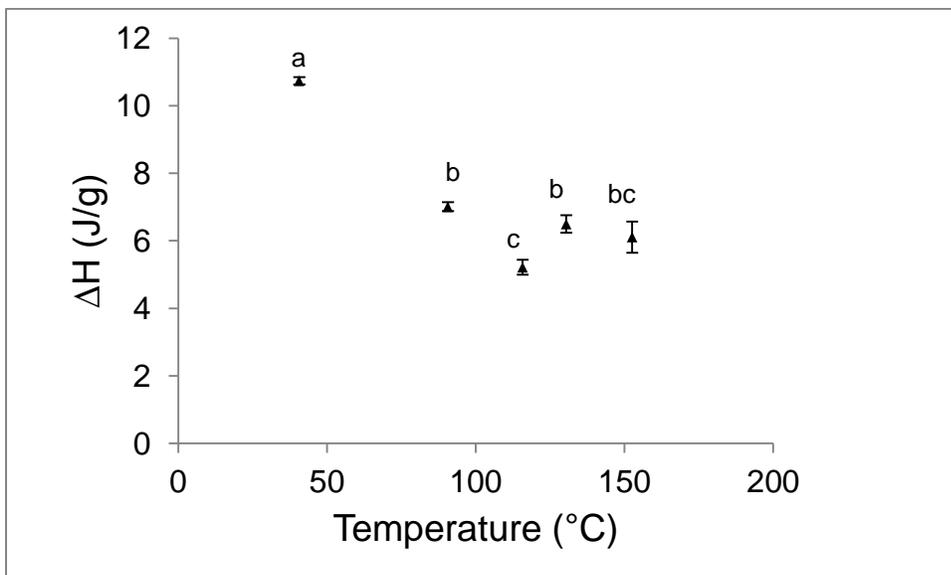


Figure 5.4 DSC enthalpy values for gelatinization of starch isolated from dough, partly baked and fully baked crackers versus internal temperatures achieved during baking (Data having the same letter are not significantly different at 95%)

5.3.3 Thermal Properties

Evaluation of DSC thermograms of isolated starch showed two endotherms for each sample regardless of degree of baking. Enthalpies of the first endotherm (representing gelatinization) plotted against the internal temperature achieved in the crackers (Figure 5.4) showed a large decrease in enthalpy to 65% of the enthalpy of the dough at the first sampling point within the oven. With further baking to sampling point 2, the enthalpy dropped to 49% that of the dough. Starch sampled from later in the process and that had experienced higher temperatures displayed higher enthalpies of 61% and 57%, respectively, compared to that of dough. As the internal temperature achieved in the crackers was the same for the last two oven sampling points as at the exit, only the exit sample data is shown.

For the amylose-lipid complex transition, enthalpy increased following baking, with the value obtained from fully baked crackers being significantly greater than that from unbaked dough (Table 5.1).

Table 5.1 Amylose-lipid complex transition enthalpy in starch isolated from dough and partly-baked and fully-baked crackers with internal temperatures achieved during baking

Location in Oven	Internal temperature (°C)	ΔH (J/g)¹	Std Dev
Entrance	40.7	1.88c	0.67
1	90.7	2.79abc	0.04
2	115.8	2.63abc	0.41
3	130.4	2.30bc	0.09
Exit	152.6	3.54ab	0.26

¹Means followed by the same letter are not significantly different at 95%

5.3.4 Crystallinity

X-Ray diffraction measurements were made of starch isolated from cracker dough (Entrance), partly baked crackers (Oven Sampling Point 1) and from starch isolated from fully-baked crackers (Exit). Diffraction patterns characteristic of A-type cereal starches i.e. peaks at 15, 17, 18, 20 and 23°, were observed in starch from all cracker samples (Figure 5.5), although the fingerprint peaks were reduced. The peak at 20° 2- θ also increased slightly in the final baked products compared to the dough.

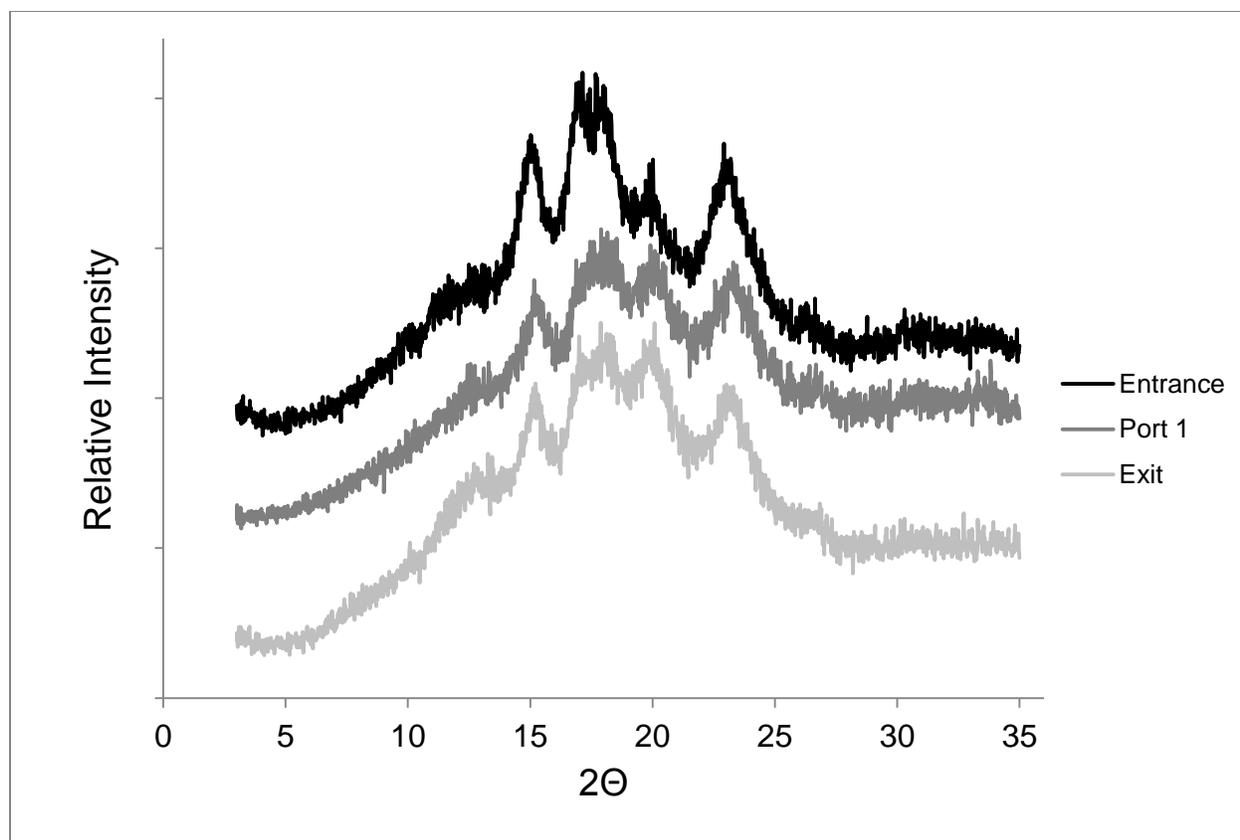


Figure 5.5 X-Ray diffraction patterns of starch isolated from cracker dough, partly baked and fully baked crackers. Diffraction patterns are offset for clarity

5.3.5 Starch Pasting Properties

The viscosity profiles of starches from different sampling points showed a typical curve, with slight changes in pasting temperature and with significant changes in the peak and final viscosities (Appendix B). The peak viscosity was plotted against the internal temperatures achieved in the crackers during baking (Figure 5.6). At the first sampling point within the oven, there was a large and significant drop to a peak viscosity of only 42% of the peak viscosity observed for the dough. At this point the cracker internal temperature was 91°C. With further baking to sampling point 2, pasting viscosity was reduced to 29% that of the dough. However, starch sampled from later in the process,

and that had experienced higher temperatures, resulted in higher peak viscosities of 45% and 51%, respectively, compared to that of the initial dough. As the internal temperature achieved in the crackers was the same for the last two oven sampling points as at the exit, only the exit sample data is shown.

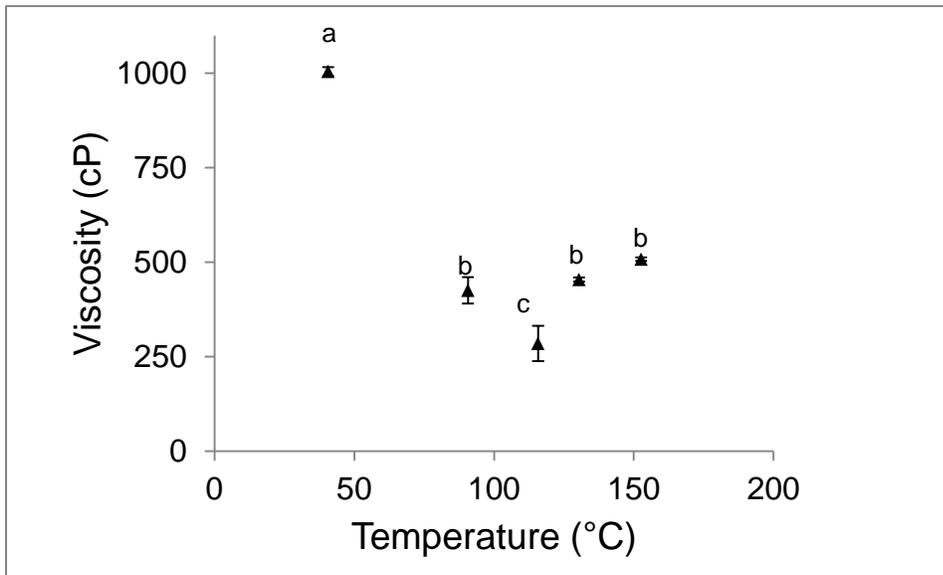


Figure 5.6 Peak RVA™ pasting values of starch isolated from dough, partly baked and fully baked crackers versus internal temperatures achieved during baking (Data having the same letter are not significantly different at 95%)

5.4 Discussion

The objective of this work was to characterize the transformations that occurred to starch in snack crackers as they were baked in an industrial oven. The observations showed that changes to starch in crackers are different from that observed in other low-moisture products such as cookies. However, the changes are not as extensive as in a high-moisture baked product such as bread. In cookies there were no statistically significant changes to granule crystallinity, pasting behaviour or gelatinization enthalpy, although there was evidence of limited granule swelling and loss of birefringence, and damage to some A-type starch granules (Chapter 3). Conversely, in bread it has been reported that gelatinization in the crumb will be almost complete, and this is accepted as an indicator of baking quality (Zanoni, Peri, Bruno, et al., 1995). Differences in starch gelatinization between crackers, cookies and bread can be seen by comparing the extent of gelatinisation (α), which can be calculated from DSC data as shown in equation 2:

$$\alpha = 1 - \frac{Q_t}{Q_{max}} [2]$$

where Q_t is the enthalpy for the baked sample and Q_{max} is the enthalpy for the raw dough (Zanoni, Peri, Bruno, et al., 1995). As shown in Table 5.2, the extent of gelatinization in snack crackers was intermediate to that of cookies and bread.

Table 5.2 Extent of starch gelatinization in baked goods of varying moisture content

Product	Moisture of dough (% d.b.)	Calculated gelatinization extent	Data source
Snack cracker	35	0.43	Chapter 5
Cookie	20	0.16	Chapter 3
Bread	~70	1.00	Zanoni et al., 1995

The single largest difference in formulation between these products is the available moisture content in the dough. However, there are other important differences in the formulations between cookies, crackers and breads. More importantly the kinetics of baking, i.e. differences in processing times, temperatures and related oven conditions, likely contribute to a larger extent to the variations in how starch behaves in these products defining final product attributes. Further, the dry basis moisture content indicated in Table 5.2 must be interpreted in light of the amount of water in the dough that is available for starch gelatinization/transformation. Competition for water in a comparatively high sugar dough such as in cookies means that there is effectively less water available to participate in reactions than the already low ~20% d.b. available (Chapter 3). In the case of bread, water is not a limiting factor in gelatinization (Mondal & Datta, 2008). However, in crackers the intermediate amount of water available is much lower than in bread and this decreases rapidly as baking progresses. Moisture was initially removed from the surface of the cracker dough piece as a result of the rapid increase in temperature in the oven, which reached 100°C within 14 s (Figure 5.1). A decrease in the rate of moisture loss between sampling points 2 and 3 was likely due to

the time required for the heat to be conducted to the interior of the cracker, since the cracker internal temperature only reached 100°C after 63 s of baking. Less moisture loss between points 2 and 3 also reflected the additional time required for mass transport of water from the interior of the cracker to the surface, as well as the requirement for latent heat of vaporization of water at 100°C to be overcome.

Resumption of rapid moisture removal also was likely slowed slightly by case hardening of the cracker surface between points 3 and 5. Moisture loss and case hardening were accompanied by typical changes in surface colour, i.e. initial lightening, followed by darkening as Maillard reaction products accumulated (Chevallier et al., 2002). The initial lightening effect seen has been explained as a result of cracker spring early in baking, i.e. thickness increases and the increased surface appears lighter (Broyart, Trystram, & Duquenoy, 1998).

These changes at the macro level during baking were accompanied by micro level transformations in starch. Microscopic examination showed that the majority of A-granules in crackers were swollen (Figure 5.3) and were no longer birefringent by the end of baking (Figure 5.2), and that only a small number of these granules remained unaffected. This differed from cookies in which the majority of A-granules did not swell and also remained birefringent (Chapter 3), i.e. heat and available moisture in cracker baking resulted in partial gelatinization, while in cookies it did not. Further evidence of gelatinization in crackers was shown by the decreased enthalpy in the DSC. The remnant enthalpy measured in the DSC is likely mostly from the ungelatinized B-granules and some ungelatinized A-granules. Although the internal temperature of the cracker had reached close to 100°C by sampling point 1, the moisture content of the

cracker had decreased to about 20%. This would explain the continued presence of ungelatinized granules. The slight increase in enthalpies at later stages of baking is likely due to some reorganization of chains due to higher internal temperatures, with a consequent increase in polymer mobility, i.e., this may be similar to what has been reported for annealed wheat starches (Jacobs et al., 1998).

The presence of ungelatinized granules is also reflected in the X-ray spectra wherein the fingerprint A-type crystalline packing is still evident in the final product, albeit with a decrease in peak intensity for all peaks. The increase in peak at $20^\circ 2-\Theta$ in the final product reflects an increased amount of single helical complexes, likely due to amylose chains complexing with lipids and surfactants present in the formulation. This increased amylose-lipid complex melting enthalpy observed in the final product also supports this observation (Table 5.1). However, this is likely because of the formation of amylose-lipid complexes within the cracker matrix, since the internal temperature of the cracker at this point was above 90°C . Eliasson, Carlson, Larsson, & Lund, (1981) also have reported that the formation of amylose lipid complexes reduces peak viscosity.

The occurrence of such a large reduction in peak viscosity by the first two in-oven sampling points was not expected. However, this observation corresponded with the high internal temperatures in the crackers (Figure 5.1), the loss of birefringence in some A-granules (not shown), and a significant increase in A-granule size (Figure 5.3). That is, pasting of A-granules was found to occur early in the cracker baking process and would have continued but for the removal of the water necessary for its continuation (Figure 5.1). A further contributor to the lower peak viscosity was the difference in maximum peak viscosity typical for each granule population. This effect was shown by

Kim & Huber, (2010), who segregated wheat A and B granules, and assessed their pasting properties. A-granules achieved approximately twice the peak viscosity of B-granules (~460 RVU vs. ~225 RVU). The partial gelatinization of A-granules in the cracker starch, which make up a larger fraction by volume of wheat starch and therefore contribute more to the peak viscosity, would result in the observed proportionately greater loss in peak pasting ability.

5.5 Conclusions

Dough temperature had been raised sufficiently by the first oven sampling point that granule swelling and associated changes had begun to occur. Beyond this point, moisture depletion began to inhibit polymer mobility and further starch transformation. The changes that occurred to starch in crackers were similar to the early stages of gelatinization in bread, but these were arrested. The placement of these changes early in the baking process increases knowledge of the development of low-moisture baked goods, and may present opportunities for manufacturers to create crackers with unique properties. This study also highlighted the large differences existing within the category of low-moisture baked goods.

The significant moisture removal from the dough pieces within the first two oven sampling points and the increase in internal temperature to over 100°C in this same period explained the observed changes (swelling, reduced pasting ability, drop in enthalpy and loss of crystallinity) in the starch granule populations. Further studies are required to relate this to textural attributes.

Chapter 6 Isotheric Heat of Sorption of Low-Moisture Dough Products

6.1 Introduction

The removal of moisture from foods is one of the oldest and most energy intensive forms of food preservation practised (Ratti, 2001). It is also an important characteristic of the baking process of low-moisture products such as cookies and crackers, as it promotes a longer shelf-life. The term 'biscuit', meaning baked twice, reflects the historic practice of returning cookies to the oven after an initial bake to ensure this drying has occurred (Manley, 2000).

Determining how much energy is required for baking is made difficult by the large amount of variation in baking processes. Oven design, the type of energy used and product formulation all contribute to variability in energy demand (Le-Bail et al., 2010). For cookie baking, a conventional deck oven used 38.24 kJ in an 11.5 minute baking process (42.97 kJ per kg of dough) (Heist & Cremer, 1990). However, not all of the energy consumed by an oven is actually used to provide heat to dough for baking transformations. Estimates of energy distribution from seven continuous ovens, baking various products, attributed only 3-11% of the energy used by the ovens to heating of dough (Trystram, Brunet, & Marchand, 1989). Much of the energy being consumed was found to be lost by conduction through oven walls and out of extractor vents as a result of the need to remove moist air from the processes. Comparison of energy demand is also challenging as it depends upon the mass considered, before or after baking, for example.

In order for the efficiency of baking processes to be improved, it is necessary to determine the minimum energy required for each part of the process. A first step toward this is to find out how much energy is needed to dry the dough to completion. In particular when reaching the domain of low-moisture content at the end of baking (typically below 18-25% water d.b.), the energy needed to remove water increases drastically. Water has to be vapourized and also desorbed; the cumulative energy needed for water desorption is named the isosteric heat of sorption. Determining the isosteric heat of sorption for a product allows this energy requirement to be estimated. Isosteric heat of sorption is given by equation [3]

$$Q_{st} = q_{st} + \Delta H_{vap} \quad [3]$$

where Q_{st} is the isosteric heat of sorption (kJ mol^{-1}), q_{st} is the net isosteric heat of sorption (kJ mol^{-1}), and ΔH_{vap} is the heat of vapourisation of water (kJ mol^{-1}).

The mechanism for finding the isosteric heat of sorption for any given product requires modelling of moisture isotherm data. Isotherms show the relationship between the amount of moisture in a product and its water activity at a particular temperature and pressure (Quirijns, Van Boxtel, Van Loon, & Van Straten, 2005a). Chung and Pfof (1967) determined isotherms for a number of different cereal grains and their products, and an example of an isotherm for corn is shown in Figure 6.1.

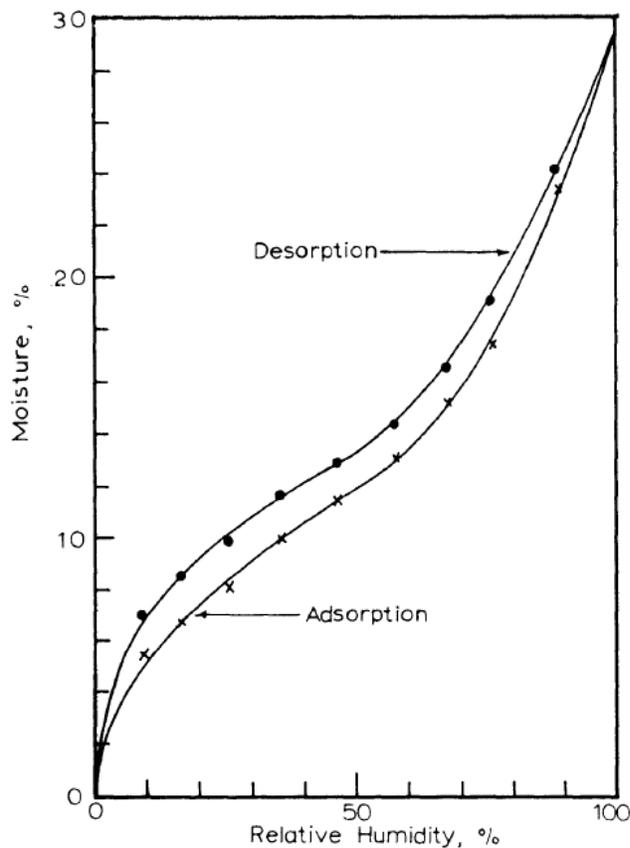


Figure 6.1 Adsorption-desorption isotherms of corn at 22°C showing hysteresis effect (Chung & Pfof, 1967)

The corn isotherm is a type 2 or sigmoid (S-shaped) isotherm according to the scheme of five types of isotherms described by Brunauer, Deming, Deming, & Teller, (1940). Type 2 isotherms are characteristic of biological and food materials (Blahovec, 2004). The shape of an isotherm is a reflection of the state of water in the product, and provides an indication of the strength and mechanism with which water is bound (Quirijns et al., 2005a). The isotherm can be divided into three regions corresponding to the stages of the water sorption mechanism (Figure 2.2) (Furmaniak et al., 2009). The three regions are referred to as regions A, B and C, region A being that of lowest water

activity in which water is adsorbed as a monolayer and does not freeze, region B having multilayer (or polymolecular) sorption, and region C having the highest water activity with water present as capillary condensation (Lewicki, 1997). As shown in Figure 6.1, the shape of the isotherm differs depending upon whether it has been obtained by adsorption or desorption. This effect, called hysteresis, is seen in all foods (Chung & Pfost, 1967). The extent of hysteresis is related to the availability of favourable polar binding sites for water molecules, and this property changes during processing as structural and conformational transformations occur (Arslan & Togrul, 2005).

Because baking is a drying process, desorption data is used in determining the isosteric heat of sorption. The energy required for desorption has been found to be consistently higher than that for adsorption. This is because desorption of previously adsorbed water requires additional energy to break the intermolecular attractive forces between sorption sites and water molecules (Moraes et al., 2008). Desorption data for modelling must be obtained experimentally for each food studied because complex interactions between food composition and structure make the mathematical determination of desorption values very difficult (Moraes et al., 2008). The effects of temperature on mobility of water molecules and on the equilibrium between vapour and adsorbed phases on desorption isotherms must be accounted for. This requires that data used to model the drying that occurs during baking should be collected at the elevated temperatures found during baking (Kumar, Singh, Patil, & Patel, 2005). Additionally, sorption data must be obtained at several temperatures in order to allow modeling, as sorption isotherms are temperature dependent, i.e. high temperatures decrease molecular binding energy, and

must be included in the model (Andrieu, Stamatopoulos, & Zafiropoulos, 1985; Quirijns et al., 2005a).

There are a number of equations that can be used for modeling of sorption isotherm data. The most commonly used equation for food isotherms is that of Guggenheim, Anderson and De Boer (GAB), equation [4].

$$\frac{X}{X_m} = \frac{C_G K a_W}{(1 - K a_W)(1 + (C_G - 1)K a_W)} \quad [4]$$

The GAB model has been shown to be a good fit for isotherms of food data up to a water activity of 0.9 (Lewicki, 1997). This model assumes the first layer of water is a tightly bound monolayer, and that later layers (2 through 9) have decreasing levels of interaction with the adsorbant surface. Water molecules beyond these layers have properties increasingly similar to those of bulk water (Quirijns et al., 2005a). Three of the parameters of the GAB equation are based on physical properties. These are: C_G , K and X_m , as shown in equations [5-7].

$$C_G = C' \exp\left(\frac{H_m - H_l}{RT}\right) \quad [5]$$

$$K = K' \exp\left(\frac{H_l - H_e}{RT}\right) \quad [6]$$

$$X_m = X' \exp\left(\frac{X''}{RT}\right) \quad [7]$$

C_G indicates how strongly water molecules are bound to the primary binding sites. A large value of C_G corresponds to stronger binding and a greater difference in enthalpy between monolayer and multilayer binding. K is a factor that corrects for the properties of the multilayer molecules relative to the bulk water molecules. When K is close to 1, the multilayer and bulk water molecules are very similar. As K decreases this indicates that the water molecules are more organized in a multilayer. X_m indicates the availability

of active sites for water sorption, i.e. the monolayer moisture content (Quirijns et al., 2005a; Quirijns, van Boxtel, van Loon, & van Straten, 2005b).

Modeling of the isotherm data to calculate values of the GAB equation parameters X'' , C' , H_m-H_b , K' and H_f-H_e can be done using a nonlinear equation solving program such as Solver (Frontline Systems, Inc.).

Following modeling of desorption isotherm data, it is possible to apply the Clausius-Clapeyron equation [8] to the optimized desorption isotherms to find Q_{st} the isosteric heat of desorption.

$$\left(\frac{\partial \ln P}{\partial \frac{1}{T}} \right)_m = \frac{Q_{st}}{R} \quad [8]$$

This requires rearrangement of the Clausius-Clapeyron equation, and subsequent plotting of the parameters $\ln(a_w)$ versus $1/T$ (Hamdami, Monteau, & Le Bail, 2004).

Determination of the slope of this relationship by use of a least-squares analysis gives q_{st} , the net isosteric heat of desorption (Quirijns et al., 2005a).

The aim of this experiment was to establish desorption isotherms for two different low-moisture baked products (cookies and crackers) at elevated temperatures and from these, calculate their net isosteric heats of desorption.

6.2 Materials & Methods

6.2.1 Sample preparation

Crackers

Snack crackers for this experiment were prepared and baked using the ingredients, formulation and method as per the Materials and Methods section detailed in Chapter 4.

Cookies

Cookies were prepared following the AACC International Method 10-53.01 “Baking quality of cookie flour – Macro wire-cut formulation”. The flour was “Francine” brand, Type 45, containing 8.8% protein. Dough was rolled to a 4-mm thickness and cut into circles using a 6-cm hand cutter. Baking took place in the benchtop PT oven, described in the Materials and Methods section of Chapter 4. The oven was equilibrated to 158°C prior to baking. Dough was placed in the oven and baked at a 158°C setting for 90 s. The temperature setting was then increased to 180°C over a 20 s period and cookies remained in the oven until the completion of the 406 s baking time.

6.2.2 Apparatus & Procedures

The sorption apparatus described by Jury (2007), and based on that of Bassal, Vasseur, & LeBert, (1993), was used for determination of the desorption isotherms. A schematic of the apparatus is shown in Figure 6.2. The apparatus was assembled in a laboratory at ONIRIS, Nantes, France.

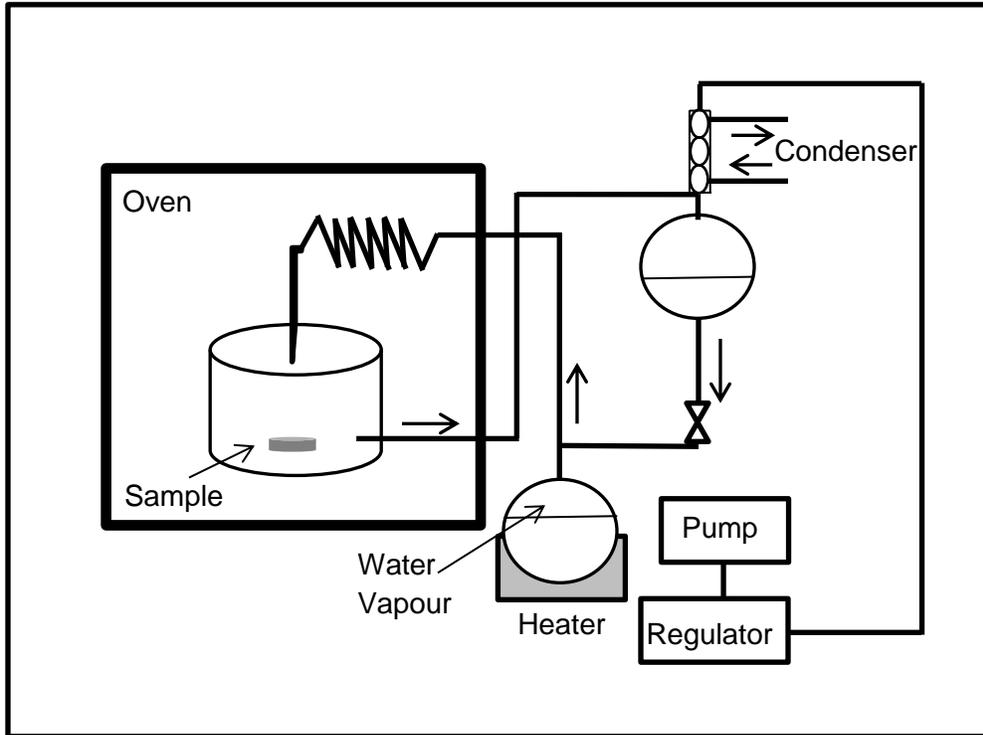


Figure 6.2 Apparatus for experimental determination of desorption isotherms

Cookie and cracker samples (approximately 2.6 g each) were placed in a pressurized glass jar inside a temperature controlled cabinet (Vötsch VC 7018, Reiskirchen-Lindenstrath, Germany) and left to equilibrate for 72 hours. It has been determined in previous work that equilibrium was reached between the sample and the moisture in the ambient atmosphere after 72 hours (Jury, 2007). Samples were stored in the jar at three different temperatures (100, 120 and 140°C) and pressure was varied at each temperature in an atmosphere of saturated steam. Pressure in the system was controlled by a Sentronic D controller (Joucermatic, France) and the pressure value was monitored using an in-line pressure gauge (Endress and Hauser, France) while being maintained to within 0.1 bar absolute. Using the pressure values and saturated vapour pressure at each temperature, as shown in Table 6.1, the relative humidities were calculated as per equation [9].

$$\text{Relative Humidity} = \frac{\text{the actual vapour pressure} \times 100\%}{\text{the saturated vapour pressure at that temperature}} \quad [9]$$

Samples were weighed following equilibration, and then dried at 105°C for 24 hours in a drying oven before being reweighed. This data was used to calculate water content (g/g d.m.) for each set of samples. Relative humidity values were converted to a_w values for each set of samples ($a_w = \text{relative humidity}/100\%$). The calculated water content and a_w data were used to plot experimentally-derived moisture desorption isotherms.

Table 6.1 Equilibration temperatures and pressures for cookie and cracker isotherm determination

Temperature (°C)	Vapour Pressure of Water (kPa)	Pressure (bar)	Relative Humidity %
100	101.42	0.912	90
		0.507	50
		0.304	30
		0.101	10
120	198.67	0.794	40
		0.596	30
		0.397	20
		0.099	5
140	361.53	0.904	25
		0.723	20
		0.361	10
		0.181	5

6.2.3 Modeling of Desorption Isotherms

The experimental moisture and a_w data were modeled using the GAB equation [4] and the effect of temperature were accounted for by incorporating the parameters C_G , K and X_m as temperature dependent variables, as per equations [5-7]. The Excel plugin, Solver, was used to determine the six GAB parameters X' , X'' , C' , H_m-H_b , K' and H_l-H_e for each temperature individually and also for the three temperature values simultaneously.

6.2.4 Isosteric Heat of Desorption

The determination of net isosteric heat of desorption for each product was achieved by taking the estimated a_w values from the three modeled isotherms at specific moisture contents, then plotting $\ln(a_w)$ versus $1/T$ and determining the slope. The a_w values of

cookies and crackers at different moisture contents are shown in Appendix C. As per equation [8], this value was then multiplied by R to give the net isosteric heat of desorption.

6.3 Results & Discussion

6.3.1 Experimental isotherms

The experimentally determined desorption values and corresponding modeled moisture isotherms for cookies and crackers are shown in Figures 6.3 and 6.4, respectively. The modeled isotherms were developed using the parameters X' , X'' , C' , $H_m - H_l$, K' and $H_l - H_e$ calculated from collected data. Specific values for these parameters are shown in Tables 6.2 and 6.3.

Table 6.2 Modeled parameters of the GAB equation for cookie.

Temperature (°C)	X'	X''	C'	$H_m - H_l$	K'	$H_l - H_e$	r^2
100-140	9.23×10^{-6}	3.78×10^4	8.39×10^5	-4.00×10^3	2.36×10^5	-3.91×10^4	0.98
100	4.71×10^{-1}	5.85×10^3	6.15×10^1	-5.31×10^3	1.12	-1.91×10^3	1.00
120	2.19×10^{-1}	4.99×10^3	5.87×10^5	-8.00×10^3	2.82	-2.00×10^3	0.99
140	2.35×10^{-2}	1.00×10^4	8.39×10^5	-1.00×10^3	4.21	-1.22×10^3	0.94

Table 6.3. Modeled parameters of the GAB equation for cracker.

Temperature (°C)	X'	X''	C'	$H_m - H_l$	K'	$H_l - H_e$	r^2
100-140	8.09×10^{-6}	3.78×10^4	8.39×10^5	-4.00×10^3	2.36×10^5	-3.91×10^4	0.98
100	5.05×10^{-1}	7.82×10^3	6.05×10^1	-6.11×10^3	4.85×10^{-1}	-2.51×10^3	0.98
120	1.43×10^{-1}	4.55×10^3	1.79×10^5	-2.65×10^4	2.75	-1.01×10^3	0.99
140	2.10×10^{-2}	8.57×10^3	8.39×10^5	-1.00×10^3	4.72	-1.26×10^3	0.98

The modeled isotherms (Figures 6.3 and 6.4) were closest in shape to the type 2 sigmoidal curves typical of most foods, particularly those that have been dried (Labuza, 1984). The effect of increasing temperature on these desorption isotherms can clearly be seen at $a_w < 0.4$, where, as temperature increased, there was a marked decrease in sorption capacity at constant a_w . This effect is common in foods. It is caused by higher temperatures leading to greater molecular excitation, which increases molecular distance and thus decreases intermolecular attractive forces. This results in less water sorption (Arslan & Togrul, 2005). The influence of temperature was also shown to decrease as a_w increased above 0.4. This second effect has also been observed in high temperature (up to 90°C) desorption isotherms of extruded pasta by Andrieu et al., (1985).

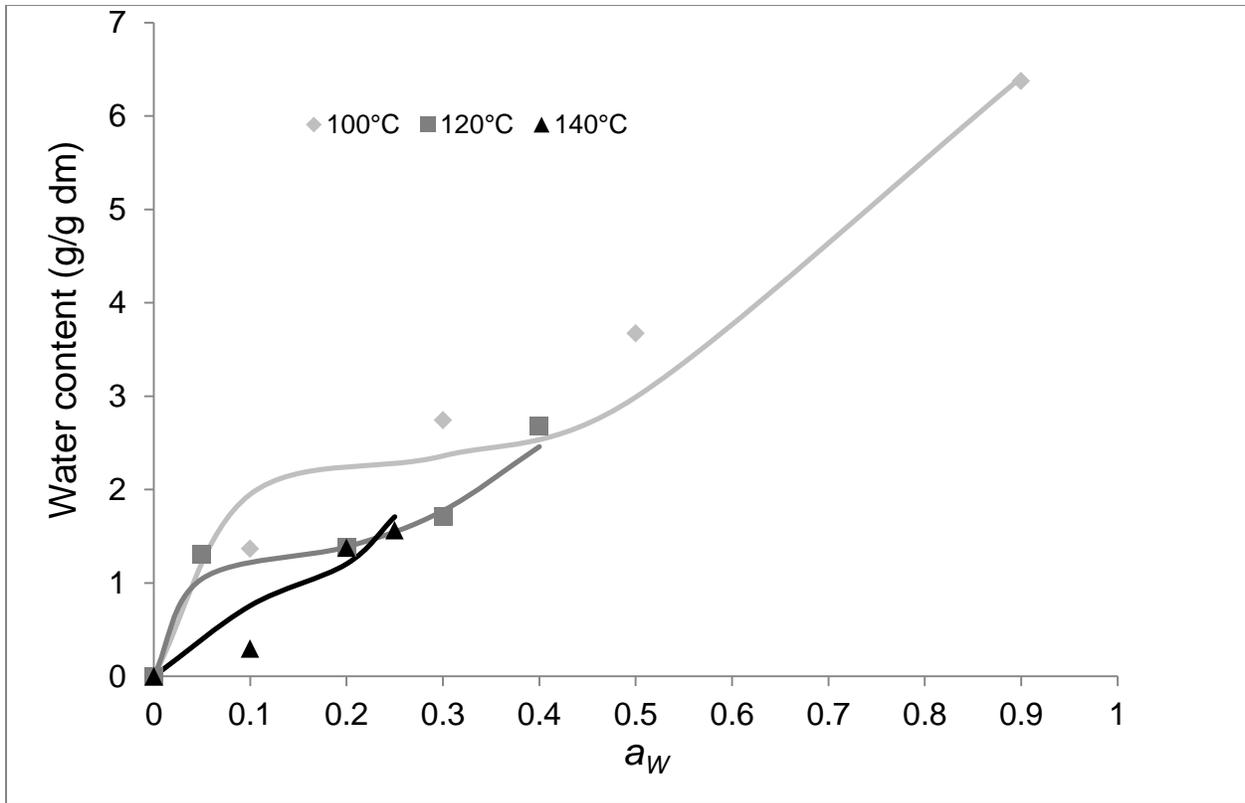


Figure 6.3 Experimental and modeled desorption isotherms for cookie (lines indicate modeled data)

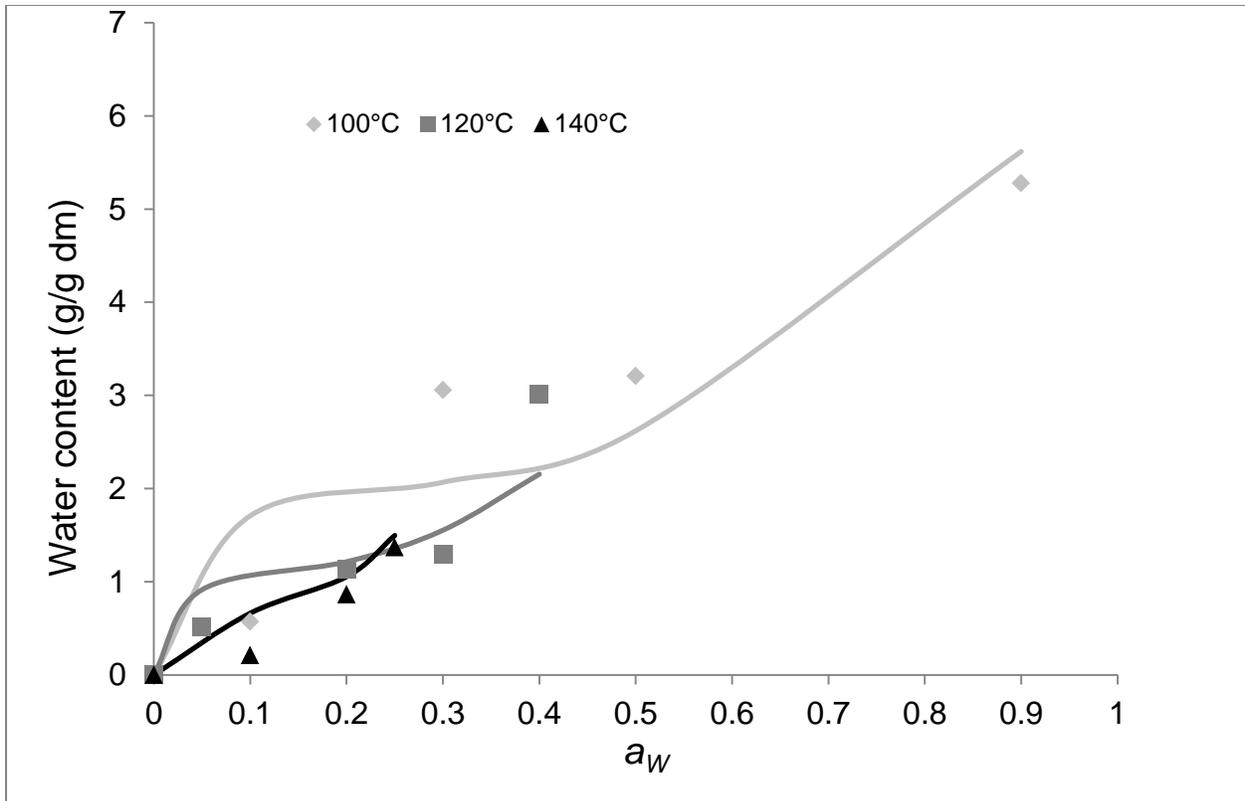


Figure 6.4 Experimental and modeled desorption isotherms for snack cracker (lines indicate modeled data)

6.3.2 Isosteric heat of desorption

Isotherm data was used to calculate net isosteric heat of desorption (q_{st}) and the values obtained for both cookies and crackers were plotted against moisture content as shown in Figure 6.5. The maximum values obtained (at 1.3% moisture d.b.) were in line with the maximum net isosteric heat values for similar food products, examples of which are given in Table 6.4.

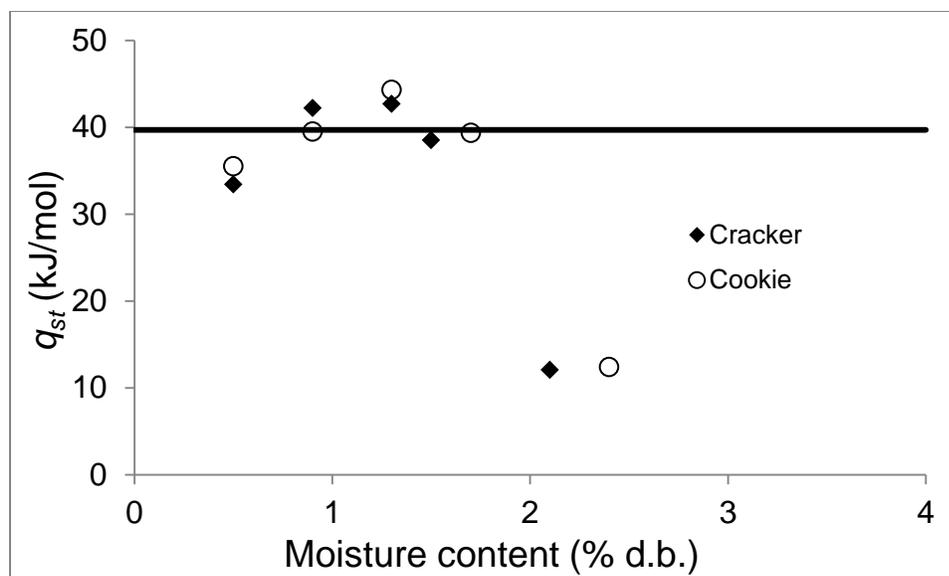


Figure 6.5 Net isosteric heat of desorption versus moisture content for cookies and crackers. Line indicates latent heat of vaporization of pure water at 120°C (mean temperature of data collection).

Table 6.4 Maximum net isosteric heat values for a range of foods

Product	Moisture content (g/100 g d.m.)	Net isosteric heat (kJ/mol)	Adsorption / Desorption	Temperature range (°C)	Reference
Macaroni	1	12 ¹	Desorption	25-45	(Arslan & Togrul, 2005)
Gingerbread	3.5	21	Adsorption	20-30	(Cervenka et al., 2008)
Wheat flour	7	20	Adsorption	41-50	(Iglesias, Chirife, & Fontan, 1989)
Biscuits	2.5	21	Adsorption	25-40	(Sampaio et al., 2009)

¹ Value inferred from Fig.7. Arslan & Togrul (2005) where $Q_{st} = 56$ and $\Delta H_{vap} = 44$.

For cookies, the maximum q_{st} value was 44.3 kJ/mol, and for crackers it was 42.7 kJ/mol. These values were higher than those found for macaroni (12 kJ/mol) by Arslan & Togrul, (2005). The lower q_{st} value for macaroni indicates a lower number of polar sites available to bind water than found in cookies and crackers. A greater number of binding sites in cookies and crackers could be due to the presence of sugars, which are strongly hydrophilic, in their formulation, and which are not typically an ingredient of pasta. Conversely, the use of egg in pasta would increase the protein content and reduce the number of sites available to bind water.

Comparisons of the maximum net isosteric heats of adsorption for wheat flour, biscuits and gingerbread gave values of 20-21 kJ/mol (Table 6.4). These values were similar to, but lower than, those for desorption values for the cookies and crackers evaluated in this study.

Gingerbread and biscuits are baked products having a similar composition to the studied products, and wheat flour is a major ingredient common to all of these products. The lower q_{st} values reflect that these were obtained from adsorption isotherm data rather than desorption data. Desorption values are consistently found to be higher than adsorption values, a consequence of hysteresis (Chung & Pfost, 1967; Tsami, Maroulis, Marinos-Kouris, & Saravacos, 1990). This effect is due to the desorption of water which has been previously adsorbed to the product surface and which requires additional energy to break attractive intermolecular forces between the sorbed water and sorption sites (Moraes et al., 2008).

It has been shown previously that values for q_{st} decrease significantly as moisture content increases and eventually approach the heat of vaporization of pure water (Wang & Brennan, 1991). In the current study the maximum moisture contents for which q_{st} values were determined were 1.7% d.b. for cookies and 1.5% d.b. for crackers. This is because high temperatures were used in the experiment in order to determine the isotherms. Researchers rarely approach such high temperatures during determinations of a_w , and typically use temperature ranges similar to those shown in Table 6.4. Such temperatures are commonly required for drying processes. The focus of the current experiment is to understand a_w , and thus

energy requirements, during the baking process, a context in which higher temperatures of up to 150°C are typical. Such an approach has been used successfully by Bassal et al., (1993) to determine a_w in microcrystalline cellulose and potato starch between 100 and 150°C. These high temperatures and corresponding low-moisture contents of the 140°C desorption isotherm precluded calculation of q_{st} at moisture contents above 1.5% d.b. for crackers and 1.7% d.b. for cookies. However, an estimate of q_{st} at a higher moisture level was determined by taking values from the 100°C and 120°C isotherms. This was done using moisture values of 2.4% d.b. for cookies and 2.1% d.b. for crackers. Net isosteric heat values of 12.38 kJ/mol for cookies and 12.06 kJ/mol for crackers were obtained, indicating that less energy would be required to remove moisture at these higher moisture contents.

The q_{st} values in Figure 6.5 for both products showed a similar pattern of decreasing q_{st} as the moisture levels dropped below 1% d.b. While this is not typical, and most research shows q_{st} values for desorption processes increasing to the lowest moisture values measured (Clemente et al., 2009; Lim, Tang, & He, 1995; Mulet, Sanjuán, & Bon, 1999; Sanchez, San Juan, Simal, & Rossello, 1997), this phenomenon has been observed previously by Moraes et al., (2008) in apples, and by Maskan & Gogus, (1998) in mulberries. It is hypothesized that this effect was due to a reduction in the forces between water molecules in the monolayer. Quirijns et al., (2005a) has stated the monolayer may consist of individual and clusters of water molecules, and that the attractive forces between water molecules in the monolayer clusters increase their energy requirement for desorption. However, as moisture content decreases, these attractive forces disappear. This results in a decrease in q_{st} at very low-moisture levels.

6.4 Conclusions

Low-moisture baked products (cookies and crackers), were shown to have similar q_{st} values with the maximum for each being 44.3 and 42.7 kJ/mol respectively. These values were found to be in line with previously published net isosteric heat data for food products. While most q_{st} research is concerned with establishing energy requirements for drying processes, the current study found that energy requirements at the high temperatures necessary to produce a baked product were similar. This information provides detail on the minimum energy requirements for drying, one of the most important parts of the baking process. It also represents one of the few examples of data from food system isotherms studied at $>100^{\circ}\text{C}$, with the measurements of a_w in cellulose and potato starch by Bassal et al., (1993) being an exception. While the current study contains novel estimates of q_{st} values in food products, further work is recommended to explore the effects that such elevated data collection temperatures may have on the water binding properties of the samples studied, as this may be a potential limitation of the current method.

Chapter 7 Conclusions & Recommendations

The objective of this research was to develop a better understanding of the transformations that occur in low-moisture dough products as they are baked. This objective was approached with the knowledge that current literature had extensively covered all of the likely physical and chemical changes that occur when heat is applied to low-moisture dough. Similarly, the literature on the engineering aspects of baking comprehensively describe the energy inputs required for the necessary heat and mass transfer of baking to occur. Yet, connections between engineering inputs and baking outcomes in low-moisture dough remain to be made. This knowledge gap is evident in industry, where tightly controlled processes are run with minimal understanding of the moment-to-moment conditions within the oven and of the effects of those conditions on the product being baked. For this reason, the approach of “process mapping” was adopted for this research. Process mapping is defined here as assessing the conditions that exist within an oven, and then using this data to interpret product transformations. Two very different baking processes were evaluated using this approach, the slow (406 s) cookie baking process in which initial dough moisture content was 19% d.b., and the faster (195 s) cracker baking process in which the initial dough moisture content was 35% d.b.

Process mapping of cookie baking revealed unexpected evidence of the effects of baking on starch A-granules. These effects included some loss of granule birefringence, disruption of granule borders, and increased gel viscosity on cooling. Assessment of AA development during cookie baking showed its development to lag behind the

development of target colour in cookies. Future work on cookie baking is recommended to investigate options for AA mediation. Specifically, it may be possible to exploit the delay in AA development by altering the final stage of the baking process, possibly by introducing an alternative drying method such as a microwave stage.

Process mapping of cracker baking revealed the importance of the early stages of baking to leavening, moisture removal and the setting up of structure in the product. The rapidity with which temperature increased in the first minute of baking was shown to be key to the changes that occurred in starch, including significant granule swelling similar to the early stages of gelatinization in bread, reduced pasting ability, a drop in enthalpy, and a loss of crystallinity. Future research on cracker baking should focus on the relationship between moisture content, heat energy and moisture removal in the early stages of baking. Interactions between these attributes was only partially captured in the current study, due to the product sampling points being spread out over the lengthy (85.3 m) bake line.

This research also contained two sub-objectives that extended knowledge of baking of low-moisture dough. The first of these was emulation of aspects of industrial baking processes at the benchtop level using a benchtop oven. While it was demonstrated that this simplified approach was not suitable for emulating most aspects of an industrial tunnel oven, it was shown to be useful for the manufacture of model products. Future work could extend the capabilities of a benchtop baking device, such that all of the parameters captured from oven profiling could be replicated. This would allow a rapid trial of an altered process without the expense and interruption to productivity that accompanies early trials on industrial ovens. The second sub-objective was

establishment of isosteric heat of desorption values for cookies and crackers modeled after those from the profiled industrial processes. The values obtained were in-line with those of previously published data, but were distinguished by being obtained at representative baking temperatures rather than from a lower temperature drying process. The similarity of values obtained for the cookies and crackers suggested little effect of formulation in this case. Future work should test this by evaluating a single product type, such as crackers, and varying an ingredient with a high affinity for water, e.g. sugar, to determine its influence.

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Appendix A



Figure A1. Model cracker dough baked in PT oven at setting of 260°C for 150 s.

Table A1. Moisture and weight of Cracker dough piece throughout baking.

Location	Entrance	Zone 2	Zone 4	Zone 5	Zone 6	Zone 7	Exit
Moisture (%) w.b.	25.95	17.84	13.04	12.37	7.98	4.75	4.93
d.b.	35	22	15	14	9	5	5
Weight (g)	3.57a ¹	2.95b	2.88b	2.77bc	2.66c	2.63c	2.83bc

¹Means followed by the same letter in each row are not significantly different at 95%

Appendix B

Table B1. Pasting parameters of cookie cracker starch throughout baking as measured using a Rapid Viscoanalyzer.

Location	Pasting temp (°C)	Peak (Pa.s)	Breakdown (Pa.s)	Trough (Pa.s)	Setback (Pa.s)	Final Viscosity (Pa.s)
Entrance	88.10c ¹	1.005a	0.654a	0.351a	0.645ab	0.994a
Sampling point 1	92.23a	0.426b	0.280bc	0.146b	0.848a	0.994a
Sampling point 2	91.7ab	0.285c	0.200c	0.085b	0.445b	0.530b
Sampling point 3	91.7ab	0.454b	0.267bc	0.182b	0.592ab	0.779ab
Exit	91.33b	0.508b	0.348b	0.160b	0.690ab	0.850ab

¹Means followed by the same letter in each column are not significantly different at 95%

Appendix C

Table C1. Equilibrium a_w of cookies and crackers at different moisture contents.

	Moisture content (g/100 g d.m.)	Temperature (°C)		
		100	120	140
Cookies	0.5	0.020	0.018	0.062
	0.9	0.037	0.035	0.130
	1.3	0.054	0.150	0.213
	1.7	0.075	0.285	0.250
Crackers	0.5	0.025	0.019	0.073
	0.9	0.042	0.047	0.160
	1.3	0.062	0.230	0.230
	1.5	0.077	0.288	0.250