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Staling of white wheat bread crumb and effect of maltogenic α-amylases. Part 1: Spatial distribution and kinetic modeling of hardness and resilience

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ABSTRACT

Bread staling is one of the most costly food deterioration processes. This study presents an in-depth, multivariate, statistical assessment of the differences in the staling process of white wheat bread as a function of storage time, usage of maltogenic α-amylases and spatial position in the loaf by texture measurements and non-linear fitting (Avrami).

This study demonstrates the effects of anti-staling enzymes upon bread staling, where significant changes in the spatial staling kinetics occur. While the spatial development of staling is reduced in the outer crumb by anti-staling enzymes, the staling is retarded in the middle. The Avrami model suggests that this happens by two different competing mechanisms: one which increases the initial staling rate, and one which slows the convergence towards the limiting hardness. The two enzyme treated breads differed widely in early and ultimate resilience, despite the fact that they were adjusted to provide the same ultimate hardness.

1. Introduction

Bread is a basic, and primary, food resource in many cultures. It contains essential constituents (e.g. carbohydrates, proteins, fibers, lipids, salts and vitamins) that collectively make bread an important resource of energy and nutrients. Bread is also an unstable, elastic, solid and complex matrix composed by the baked dough and air, creating a structure of open foam, or sponge. The solid part of the bread contains a continuous phase, composed in part of an elastic network of cross-linked gluten molecules (Shewry, Halford, Belton, & Tatham, 2002) and in part of leached starch polymer molecules (Damager, Engelsen, Blennow, Møller, & Motawia, 2010), primarily amylose, both uncomplexed and complexed with polar lipid molecules, and a discontinuous phase of entrapped, gelatinized, swollen, deformed starch granules (Aguirre, Osella, Carrara, Sanchez, & Buera, 2011; Gray & BeMiller, 2003).

The unstable bread matrix will deteriorate over time, due to staling, which presumably is responsible for the largest single source of food waste with a significant global environmental footprint. In Europe, around 39 million tons of bread was produced in 2010, 70% of which were white wheat bread (UK) and that around 40% of this bread is wasted because the bread gets hard i.e. staling. Staling is a complex process that starts soon after baking and has been defined as "a term which indicates decreasing consumer acceptance of bakery products caused by changes in the crumb other than those resulting from the action of spoilage organisms" (Bechtel, Meisner, & Bradley, 1953). The most important manifestations of staling are an increase of crumb hardness, an increase in crumbliness of the crumb, a decrease in water absorption capacity and a deterioration of "fresh bread" flavor (Gray & BeMiller, 2003; Kulp & Ponte, 1981).

Due to its importance, bread staling has been extensively studied for more than a century. The first research on staling was reported by Boussingault (1852), who showed that staling of bread is not due to loss of moisture by the drying out process and that stale bread could be freshened by moderate heating. Using X-ray diffraction, Katz (1928) demonstrated that crystallization of amylose and amylopectin (one manifestation of starch retrogradation) was responsible for the firming of bread over time. However, despite intensive research efforts the complete molecular mechanisms for bread staling remain elusive (Gray & BeMiller, 2003). Even simple bread dough formulations contain several ingredients

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and wheat flour, the main constituent of bread, contains complex families of carbohydrates, proteins and fats, as well as a large number of secondary metabolites (Khakimov, Jespersen, & Engelsen, 2014). All these various components will play a role in bread staling, as they undergo changes during the bread making process and during aging of the final product. Thus, the staling kinetics depend on a complex balance of input parameters (dough ingredients, yeast, enzymes), process parameters (mixing, proofing, baking, cooling) and storage parameters (humidity, temperature).

The main manifestation of bread staling is crumb firming and when it comes to a mechanistic understanding of this phenomena there is a general agreement that changes in the starch component (65–70% of the wheat flour) is primarily responsible for bread staling. When starch is heated up in the presence of water (baking) it will swell and, when reaching a certain temperature, it will gelatinize. During this process, the native ordered structure (crystallinity) of the starch granules will be lost and a disordered polymeric 'gel' network will be created. However, this starch gel is a metastable system and upon ageing, it will slowly recrystallize (retrograde). Staling as a primarily crystallization process is supported by the fact that the staling of bread increased as the storage temperature is decreased, which is characteristic for crystallization processes, but not commonly applied to chemical reactions (Fearn & Russell, 1982). While it was early demonstrated that drying out of the bread does not explain the staling process (Boussingault, 1852), it has been shown that the moisture content of the bread is the major factor controlling the firming rate in the bread and that the moisture content is inversely proportional to the rate of firming (Rogers, Zeleznak, Lai, & Hoseney, 1988). However, as bread age, water will migrate from the crumb to the crust and evaporate from the surface. These processes may result in water transfer from one component to another, which in turn may be a contributing factor of bread staling since the properties of gels of starch and gluten are markedly influenced by water, and since starch retrogradation is dependent on the availability of water as a plasticizer. The kinetics of moisture loss during bread baking and staling has been studied intensively by, for example, a combined in situ NMR analysis and texture profile analysis (Engelsen, Jensen, Pedersen, Nørgaard, & Munck, 2001), and more recently empirical and semi-theoretical models have been proposed for modeling moisture loss in bread (Pour-Damanab, Jafary, & Rafiee, 2013), primarily focusing on the moisture loss that occurs during baking.

Many scientific and industrial efforts are directed towards retarding the bread staling process, since substantial amounts of money, energy and food is wasted both by the consumers and by industry. Several ingredients have the potential to retard the bread staling process. Pentosans, which are a natural ingredient in the wheat flour, retard the staling process by acting as a sponge and thus increase the water absorption. Other ingredients, such as modified starches and salts will have a similar type of effect. Emulsifiers are probably the most used anti-staling agents. The mechanisms are not fully understood, but they make a complex with the amylose or amylopectin which retard, but not inhibit, retrogradation. Finally, numerous studies have indicated that the addition of amylases to bread formulations reduces the firming of bread (Miller, Johnson, & Palmer, 1953) and basically three different mechanisms have been proposed: (1) decreased starch retrogradation, (2) decreased rigidity of the starch gel network and (3) decreased starch/protein interactions. However, it is beyond any doubt that the functional effect of freshness α-amylases is primarily to act on amylopectin to form soluble low molecular weight branched chain polymers, which will be less prone to retrogradation and which will change the water availability and mobility. This will in turn have major impacts on starch gelatinization and retrogradation. Clearly, the enzymes not only have the potential to reduce production costs and increases profits, but also to improve sustainability (Whitehurst & Van Oort, 2009) by reducing the impact of manufacturing on the environment and the consumption of chemicals, water and energy and the subsequent generation of waste. Life cycle assessment studies have indicated that the use or increased use of anti-staling enzymes in bread production can lead to drastic reduction of the environmental impact (5.4 kg CO_2 per 100 breads sold) (Jegannathan & Nielsen, 2013).

This study aims at studying the inhibition of the staling kinetics of commercial white wheat bread by maltogenic α-amylases. Previously, Amero and Collar made a comprehensive study of crumb firming kinetics as a function of anti-stalling additives, using TPA and Avrami fitting (Armero & Collar, 1998). However, in their study Amero and Collar used emulsifiers, hydrocolloids and an α-amylase (Fungamyl®), which is normally added in commercial bread production to improve baking performance of the dough (i.e. to compensate for differences in the flour). Thus, to our knowledge, this work is the first to study the staling kinetics of white wheat bread with and without two different maltogenic α-amylases. Furthermore, this study aims to investigate the spatial development of the staling kinetics as a function of position in the bread and of the addition of anti-staling enzymes. Given the strong temperature gradients during baking, it is to be expected that moisture content, yeast and enzyme activities are spatially distributed in the loaf. Perhaps even more important, the starch gelatinization will be affected, which in turn will affect the starch retrogradation and amylase activity. Several methods are available for measuring staling/starch retrogradation, including X-ray diffraction, differential scanning calorimetry (DSC), infrared spectroscopy (IR) and proton nuclear magnetic resonance (NMR) relaxation, but the most widely accepted and most direct method to measure hardness and correlation to sensory evaluation is texture profile analysis (TPA) (Bourne, 1978). The TPA test consists of two successive uniaxial compressions of a bite-size piece of a food that imitates the action of the jaw. The "two-bite" TPA curve (Fig. 1) represents the evolution of the compression force as a function of time and seven basic descriptors for eating quality (Szczesniak, 1963) can be deducted from the curve: hardness, cohesiveness, elasticity/resilience, adhesiveness, brittleness, chewiness, gumminess and viscosity, of which the latter three are secondary parameters derived from the others. The mechanical properties of bread are a function of the crumb structure (Scanlon & Zghal, 2001) and in particular the bread crumb hardness has been studied extensively due to its high correlation to sensory evaluations (Carson & Sun, 2001). In this work, the focus is on two of the textural parameters obtained from the first bite, namely hardness and resilience.

In order to determine the kinetics of the staling process, it is common to fit the hardness data to the Avrami equation (Armero & Collar, 1998; Avrami, 1939; Cornford, Axford, & Elton, 1964; Russell, 1983) assuming that the staling process is a simple phase change:

$$\Theta = \frac{E_L - E_t}{E_L - E_0} = \exp(-k * t^n) \quad (1)$$

where Θ is the fraction of recrystallization still to occur, E_L is the limiting value of hardness, E_t the hardness at time t, E_0 the hardness at time zero, k is the rate constant and n is the Avrami exponent (indicative of the nucleation type and crystal growth geometry). Normally, the important rate constant is given as the time constant, $1/k$, which describes the bread firming rate (i.e. the higher number, the slower the firming process). Data from fitting of hardness of bread and starch gels are in good agreement and indicate that bread staling is primarily characterized by retrogradation of the starch component of the bread crumb. The Avrami equation has previously been fitted to staling of bread using parameters derived from hardness measurements (Armero & Collar, 1998; Cornford et al., 1964;