

Objectives:

The objectives of this experiment are:

- 1) To become aware of the significant role chemistry plays in the manufacture of food products-- in particular pretzels.
- 2) To understand the Maillard browning reaction and its effect on pretzel manufacture.
- 3) To observe the effects of various solutions with different pH values on pretzel manufacture.
- 4) To compare human evaluation of sensory characteristics to that of a machine.

Methods:

The methods for the *Pretzels* experiment were followed as stated in the laboratory handout with a few exceptions. There were only two groups, each consisting of three students. Each group made two pretzels for each dipping solution. All solutions on the *Pretzels* laboratory handout were used except the 2% whey. The texture analyzer was not working, so a value for the force required to break the surface of the pretzels could not be determined. Also, a comparison between group and class data was not made.

Results:

Table.1: Individual Group Evaluation of Various Dip Solutions on Pretzel Characteristics

<i>Dipping Solution</i>	<i>General Appearance^a</i>	<i>Color^b</i>	<i>Texture^c</i>	<i>Crust Formation^d</i>	<i>Flavor^e</i>
2% Citric acid	5	5	5	5	5
2% NaOH	1	1	1	1	1
2% Na ₂ CO ₃	2	2	2	2	2
Water	4	4	4	4	4
Egg White	3	3	3	3	3

a= Number scale 1-5 with 1 being excellent and 5 being poor

b= Number scale 1-5 with 1 being the darkest and 5 being the lightest

c= Number scale 1-5 with 1 being crisp and 5 being chewy

d= Number scale 1-5 with 1 having great crust formation and 5 poor crust formation

e= Number scale 1-5 with 1 having excellent flavor and 5 having poor flavor

Table.2: Hunter Colorimeter Results for Individual Group Data on Pretzels Dipped in Various Solutions

<i>Dipping Solution</i>	<i>L^a</i>	<i>a^b</i>	<i>b^c</i>
2% Citric acid	77.03	2.19	19.93
2% NaOH	47.87	16.37	22.05
2% Na ₂ CO ₃	73.77	3.12	23.67
Water	76.63	1.82	19.98
Egg White	78.33	1.44	20.47

a= L equals 0-100 (0=black and 100=white)

b= a equals red to green (+ = red and - = green)

c= b equals yellow to blue (+ = yellow and - = blue)

Table.3: Comparison of Group Sensory Evaluation of Color and Mechanical Evaluation By the Hunter Colorimeter L-Value

<i>Dipping Solution</i>	<i>Sensory^a</i>	<i>L-value^a</i>
2% Citric acid	5	4
2% NaOH	1	1
2% Na ₂ CO ₃	2	2
Water	4	3
Egg White	3	5

a= Number scale 1-5 with 1 being the darkest and 5 being the lightest.

Discussion:

In every category, the pretzels dipped in NaOH ranked number one and citric acid pretzels ranked number five (Table.1). The NaOH pretzels had a great savory flavor. The Na₂CO₃ pretzels had a fairly decent flavor, but not as great as NaOH. Pretzels dipped in egg white tasted more like biscuits than pretzels, and pretzels dipped in water were bland. The citric acid pretzels had sour notes. For crust formation, NaOH pretzels had the best crust. It was dark, thick, glossy, and had the most even coverage. Na₂CO₃ also produced an even, brown, slightly glossy crust, but the thickness of it was not as great as the NaOH. Pretzels dipped in egg white had a crust, but it was thin and had yellow hues. Water and citric acid pretzels had very little crust formation. These crusts were dull and colorless. Pretzels dipped in NaOH had the best texture--crisp on the outside and soft on the inside. The Na₂CO₃ had a texture similar to the NaOH pretzels, except the outside was not as crisp. The egg white pretzels had a texture like biscuits--slightly chewy. Pretzels dipped in water and citric acid were chewy and stuck to the teeth. For color, NaOH pretzels had a dark, well-developed brown color and the Na₂CO₃ pretzels were a close second. Egg white, water, and citric acid pretzels had sporadic browning and the amount of brown color decreased from egg white to water to citric acid. The egg white pretzels also had more of a yellow color than all the rest because the actual solution of egg white was slightly yellow whereas the other solutions were colorless. General appearance was mainly based on

color, the presence of gloss, and crust formation. The rankings for this characteristic followed rankings for the other categories.

All of these characteristics were in some way related to the browning of the pretzel surface. Pretzels brown due to complex reactions called Maillard reactions. In the case of the pretzels, heat from the oven acted as a catalyst for the reaction of reducing sugars with free amino groups of amino acids that were part of protein chains. A compound called glucosylamine was formed, which then underwent a reaction called the Amadori rearrangement. Reactive cyclic compounds were formed as a result of the Amadori rearrangement. These reactive cyclic compounds polymerized at pHs greater than 5 to form insoluble, dark-colored, nitrogen containing compounds called melanoidins. In addition to the formation of brown color, aroma and flavor compounds are also produced as a result of Maillard reactions.

Variations in dips can be attributed to pH differences. The pH of the pretzel played an important role in forming the resulting brown color. As the pH of the dips decreased so did the browning. In Maillard browning, the available pair of electrons on the N atoms, of the free amino groups of proteins, attacks the slightly positive C atom of a reducing sugar (Figure.1). However, when the pH is too low the attack of the C atom cannot occur. This is because the lower the pH the more available H⁺ ions in solution. The available pair of electrons on the N atoms on the free amino groups binds the H⁺ ions. This causes ionization of the amino group (Figure.2) and its electrons are no longer free to react with the reducing sugars, preventing Maillard browning from occurring.

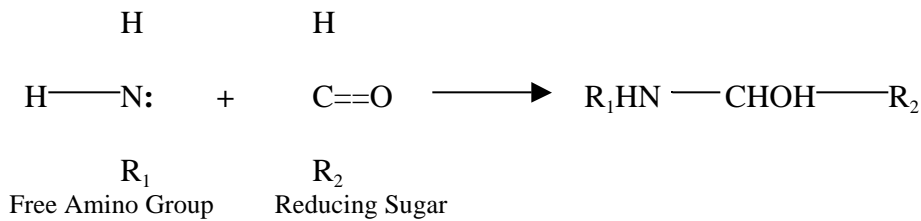


Figure.1: Mechanism of Initial Step in Maillard Browning

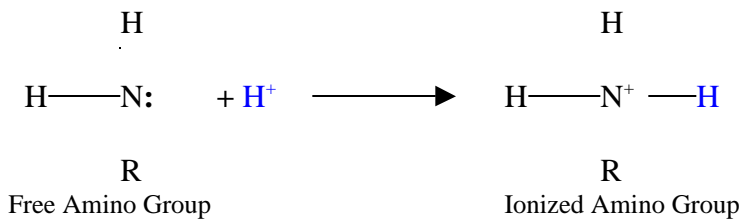


Figure.2: Mechanism for pH Effect on Browning

Dips used had a wide range of pHs. As pH increased the amount of Maillard browning increased. The dips in order from high (basic) pH to low (acid) pH are as follows: NaOH>Na₂CO₃>egg white>water>citric acid. Therefore, the order of pretzel colors, dark to light, followed the order of dips, high to low pH. The pH order held true for all characteristics, not just color (Table.1). It was the Maillard reaction that determined the acceptability of the

various pretzels. The more Maillard browning that occurred the better the flavor, texture, crust formation, and general appearance of the pretzels.

The general appearance of the pretzels was not solely based on browning. It was also based on the amount of gloss on the pretzel surface. Gloss on pretzels is desirable and is commercially formed by dipping the pretzels in a lye or caustic bath consisting of 0.5% NaOH or 2% Na₂CO₃. In this experiment gloss was formed on both NaOH and Na₂CO₃ pretzels. Like in Maillard browning, the mechanism for gloss formation is based on pH. At a neutral pH net electrostatic repulsive energy is small because most proteins are negatively charged and some are positively charged. At extreme pH values, the proteins develop a high net charge and repel each other. This causes the proteins to swell, unfold, and ultimately denature. At the alkaline pHs used in this experiment, the unfolding is even more dramatic because the carbonyl, phenolic, and sulfhydryl groups that are partially buried in the protein structure become ionized and unravel the polypeptide chain as they try to move themselves to a more favorable environment. The denaturing of proteins at the pretzels' surface, due to the high alkaline solutions of NaOH and Na₂CO₃, caused a glossy appearance.

Hunter L-values showed a large difference between the NaOH and the rest of the pretzels (Table.2). On a scale of 0-100, with 0 being black and 100 being white, the NaOH pretzels scored a 47.87 and all others scored greater than 73.77. The a-values also showed a drastic difference between the NaOH pretzels and all the others (Table.2). However, b-values for all the pretzels were within a similar range (Table.2). This was expected because shades of red and darkness coincide with browning and browning reactions. Since the NaOH pretzels browned significantly more than the others, Hunter L and a-values were significantly higher for the NaOH pretzels. All the pretzels were made from the same dough and because the dough itself had yellow hues, the Hunter b-values varied only slightly.

Hunter L-values were the same as visual scores for NaOH and Na₂CO₃ (Table.3). The Hunter L-values agreed that the water-dipped pretzel was darker than the citric acid-dipped pretzel, and by a very small amount (Table.2 and Table.3). However, for the egg white, differences existed in what was visually perceived (Table.3). Visually, the egg white-dipped pretzel appeared darker than the water-dipped. The Hunter L-value showed the egg white pretzel to be the lightest. The solution of egg white was slightly yellow in color and when the pretzel was dipped into this solution it turned slightly yellow in color. After baking, the eye may have been deceived into seeing yellow hues as "darkness." Another explanation for the discrepancies between visual and Hunter scores could be discrimination in sampling. Only a small piece of pretzel was broken off and used for the colorimeter test. What piece was chosen, and how that piece was placed over the colorimeter lens, could have effects on the reading. In this case, it was important to have nothing but the outside crust of the pretzel being read. If the tear on the pretzel was uneven, such that the inside was exposed, the Hunter colorimeter would give a higher reading than expected. To avoid this, the colorimeter test should be performed on many samples and an average should be reported. If the Hunter value had placed the egg white-dipped pretzel in between the Na₂CO₃ and water pretzels, visual scores and Hunter scores would have matched.

The significance of this experiment was that it showed the importance of chemical reactions in food product manufacture. Almost every ingredient put into food will react with other

ingredients to produce a product. Sometimes that product is desirable and sometimes it is not. Understanding the chemistry involved in the reactions between components of food allows the food scientist to go back and make an undesirable product desirable. Knowing how the Maillard reaction occurs and how it can be manipulated to produce browning and flavors is important. Consumer acceptability is based on visual appeal. In the case of pretzels, no consumer would walk into a grocery store and pick up a bag of white pretzels. They want to see the deep brown color that is characteristic of pretzels. At the other end of the spectrum, no one would purchase dried eggs they were brown in color or a loaf of bread if it was burnt. Consumers associate the presence or absence of color with quality. If the food processing company does not understand these complex chemical reactions, they will not stay in business for long.

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Questions:

1)

Functions:

Flour: The foundation of the dough. It acts as a binding and absorbing agent. It is important because it contains proteins that when hydrated form an elastic material

called gluten. Gluten is responsible for retaining the gases produced by yeasts. Flour also contains the enzymes alpha and beta amylases that break down the starch present into maltose units that can be utilized by yeast.

Beer: Adds flavor and is a source of maltose and water. Maltose supplies yeast with a food source. Since water is not listed in this recipe, beer would serve as a source of water to hydrate the proteins in the flour and form the gluten matrix.

Milk: A source of proteins and lactose. Proteins provide tightening and strengthening of dough and lactose acts as a reducing sugar aiding in the color formation (Maillard browning) of the crust. Also contains vitamins and minerals, which give some nutritional value to the pretzel. Milk also contains 86.6% water, which along with beer, hydrates the flour proteins and forms gluten.

Salt: Enhances flavor. It tightens and strengthens gluten, making dough less sticky and easier to handle. Also helps to control the speed of fermentation--without salt, yeast fermentation would be too rapid.

Shortening: Aids in dough manipulation by lubricating the strands of gluten. Dough will become soft, not sticky, and form the desired shape more readily.

2)

Each dip affected the surface of the pretzels as follows:

NaOH= Crust was well developed and covered the entire surface area of the pretzel. A rich brown color was formed and the surface had a glossy coating.

Na₂CO₃= Similar effects as NaOH, except color was not as dark and there was not as much gloss on the surface.

Egg white= Browning was very light and sporadic. There was no gloss and there were slight yellow hues.

Water= Browning only on edges or on small, raised bumps (imperfections) on dough and no gloss.

Citric acid= The same as water with even less browning.

Mechanism for Browning: Refer to Discussion section.

Mechanism for Gloss: Refer to Discussion section.

3)

The browning of the pretzel crust was caused by the Maillard reaction. Refer to the Discussion section for a detailed explanation.

Variations in dips can be attributed to pH differences. Refer to Discussion section for further explanation.

4)

The yeast was used as a leavening agent and for taste and flavor. Yeast consumed the sugar in the dough, and through a series of metabolic reactions, produced CO₂ and ethanol. The CO₂ became entrapped in the gluten matrix and caused the dough to rise, or increase in volume. Therefore, all the components that contribute to the gluten matrix including flour, water from milk and beer, milk proteins, salt, and shortening, help retain the yeast by-products. Ethanol, propanol, butanol, pentanol, and carbonyl compounds such as, acetaldehyde, propanal, butanal, pentanal, and furfural are all produced during fermentation and can contribute to aroma, taste, and flavor.

5)

The heat treatment would denature whey (or serum) proteins in the milk. Milk protein consists of mainly casein and whey. Whey proteins, alpha lactalbumin, beta lactoglobulin, serum albumin, immunoglobulins, and proteose-peptones, are globular in structure whereas caseins are non-globular and have extended structures. The difference in structure between casein and whey proteins is due to the presence of disulfide bonds. Whey proteins contain numerous disulfide bonds that stabilize their globular structure. Unlike caseins, whey proteins undergo structural changes when heated. Thermal energy will break disulfide bonds, expose hydrophobic groups, and as a result, these whey proteins will denature. In bread, it is desirable to denature these whey proteins because they restrict the foamability and volume of the loaf. Air cells formed by whey proteins are small. Caseins however, are flexible and can extend to form a high-volume foam. Bread volume is much greater than that of pretzels. The characteristic pretzel is flat compared to bread. It is undesirable to have fluffy pretzels therefore, it is not necessary to denature the whey proteins in the milk by heating it prior to making pretzels.

6)

Refer to Discussion section.