Under the Microscope

the science of browning reactions

WELCOME BACK TO ANOTHER EDITION of Under the Microscope. In the last issue we discussed the formation of acrylamide during the roasting process and briefly introduced the Maillard Reaction. This time around, we'll take a deeper look at some of the other reactions taking place and discuss a new, complex set of reactions known collectively as browning reactions. This new set of reactions affects not only coffee but a broad range of food products and their flavor development. Although the Maillard Reaction is considered one of the most important reactions to occur in food, it is only one of three browning reactions available to us. So, sit back and relax as we present to you the science of browning reactions in this month's lecture series.

continued on page 44

ENZYMATIC BROWNING

Unlike coffee roasting, which requires high temperatures to initiate, enzymatic browning reactions occur spontaneously and at room temperature. However, like all reactions occurring in nature, a source of energy is required for initial activation. In the case of coffee, the activation energy is provided by the heat created by roasters, but enzymatic reactions require the presence of a specific catalyst, or enzyme. Simply put, an enzyme is a unique protein that accelerates specific reactions. There are literally thousands of enzymes in biological systems, and without them life would come to a grinding halt. The alcohol contained in those glasses of wine we enjoyed this weekend was metabolized by none other than alcohol dehydrogenase, while the protein in our steak was broken down into smaller, more digestible fragments by pepsin—a stomach enzyme. And the caffeine that we so religiously consume every day is metabolized by a broad range of important co-enzymes called Cytochrome P450.

Although the technical name may be elusive, enzymatic browning is a phenomenon that we've all experienced firsthand. The reaction is best illustrated by taking a fresh apple and slicing it in half. As we cut through the apple's cellulose tissue, cells rupture, thereby releasing a myriad of compounds into surrounding tissue. One important compound is an enzyme

called polyphenol oxidase (PPO). Once exposed to air, the enzyme rapidly transforms colorless phenols present in the apple's tissue into a long chain of brown-colored polymeric compounds—and ultimately ruins our pristine white apple. Although the brownish hue may be unappealing to the eye, contrary to popular belief, the reaction in no way creates toxins or endangers the health of those consuming it—as long as you're not bacteria.

Just like a Russian KGB agent carries a pill of lethal cyanide with him (in the event of capture by enemies), the apple senses when it's been attacked and immediately jumps into self-defense mode. But, how? By creating the very same brown polymers we discussed. According to researchers, the brown polymer created during enzymatic browning is highly toxic to bacteria. It's Mother Nature's way of protecting the plant from bacterial infection during its latter, more vulnerable stages of ripening.

Though the benefits of enzymatic browning remain limited to only a handful of products such as raisins, plums, figs and cacao, the reaction is, for the most part, a detriment and serious quality concern. Because of its spontaneous nature, enzymatic browning represents a significant economic loss within the fruit and vegetable industry. It's been estimated that at least 50 percent of all fruit and vegetable goods are damaged due to bruising/tearing during transport to market. As such, scientists have developed relatively simple ways of inactivating enzymes and mitigating browning losses. Blanching, or essentially steaming, is useful as the heat deactivates PPO and prevents browning. Unfortunately, not all products can be subject to this. Another method involves the addition of an acid, usually ascorbic acid, to the pre-oxidized product. Many chefs, for example, add a bit of lime juice to fresh guacamole during preparation. Turns out that the decrease in pH prevent the phenols from oxidizing and thus prevent, or at least delay, enzymatic browning.

So with all this talk about enzymatic reactions you're probably wondering at this point, "So how does this relate to coffee?" Well, it doesn't. Sorry. Enzymatic reactions are only important for products such as tea and cocoa, which during post-processing serve to create flavor changes. We only mention enzymatic reactions as a formality, since any discussion on browning reactions would be incomplete

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without it. For now, think of enzymatic reactions as the boring sibling of browning reactions. And for the typical caffeine-junkie roasters, that's not enough—we need more spark and complexity! This is where we begin our next discussion of non-enzymatic reactions. This next set of complex reactions will serve to explain the bulk of the chemical changes occurring in coffee during roasting.

NON-ENZYMATIC BROWNING

Unlike the enzymatic reactions we discussed earlier, non-enzymatic reactions are significantly different. In the latter, no enzyme is required, but the reaction does require the presence of heat, sugar

continued on page 46

and amino acids. As we'll discuss in greater detail, two of the most important non-enzymatic reactions in coffee are caramelization and the Maillard reaction.

Caramelization

Caramelization is perhaps the easier of the two non-enzymatic browning reactions to describe. Simply put, caramelization is the oxidation or the thermal decomposition of sugars into color and flavors. Although any sugar can be caramelized, we typically see sucrose, or table sugar, as the sugar of choice for cooking applications. As sucrose is heated to 160° C it slowly begins to melt, losing water molecules in the process and becoming a viscous semi-transparent liquid. As heating reaches 200° C, the compounds in the molten sugar begin to rearrange, forming brown-colored caramel-like compounds and imparting its characteristic burnt caramel aroma. But this isn't your grandpa's caramel; the caramel created in this process is unlike the caramel candy we all loved as kids. This caramel is a bitter/burnt gooey compound with little to no sweetness, occasionally used as the topping on custard desserts. The caramel we eat is created by mixing sugar, milk and other flavorings, but it is produced in much the same manner as the caramel that occurs in coffee.

Depending on the heating conditions, manufacturers can shift the by-products of caramelization to either maximize the formation of aromatic compounds or colored caramel-like compounds. In the latter condition, sugar is heated in the presence of ammonia to produce high concentrations of brown-colored compounds, typically used by the cola industry for coloring.

In addition to creating aroma and color, caramelization creates a broad range of compounds including organic acids in the process. We can clearly see this, for example, in the making of peanut brittle. In the latter stages of commercial brittle making, caramelized sugar is allowed to cool and thicken, at which time baking soda and other flavorings are usually added. The baking soda then reacts with the organic acids produced during caramelization, neutralizing them to form carbon dioxide gas. This gas acts as a leavening agent, creating tunnels in the product and ultimately producing the characteristic "Swiss cheese" texture commonly found in candy brittle.

In coffee, a similar reaction occurs. As sugar is decomposed, it too produces carbon dioxide gas, which increases cell pressure within the bean, rupturing it and, ultimately, producing the audible "pop" we hear during second crack. What about first crack? Well, technically, the first crack is produced, partly, by the rapid increase in cell pressure by evaporating water—steam—during the roasting process.

Up to 90 percent of the initial sucrose is decomposed during roasting to produce a wide range of byproducts, including formic and acetic acid. Studies have shown that acetic acid concentration in model studies can increase up to twenty times its initial concentration, namely in the early part of roasting, then quickly evaporating in latter stages—due to its volatility. But acetic acid is unique in that it is a relatively weak acid, which affects perceived acidity and overall coffee quality. It's no surprise then, that with arabica containing almost twice the concentration of sucrose as robusta, we perceive a greater intensity of aroma and acidity in the cup.

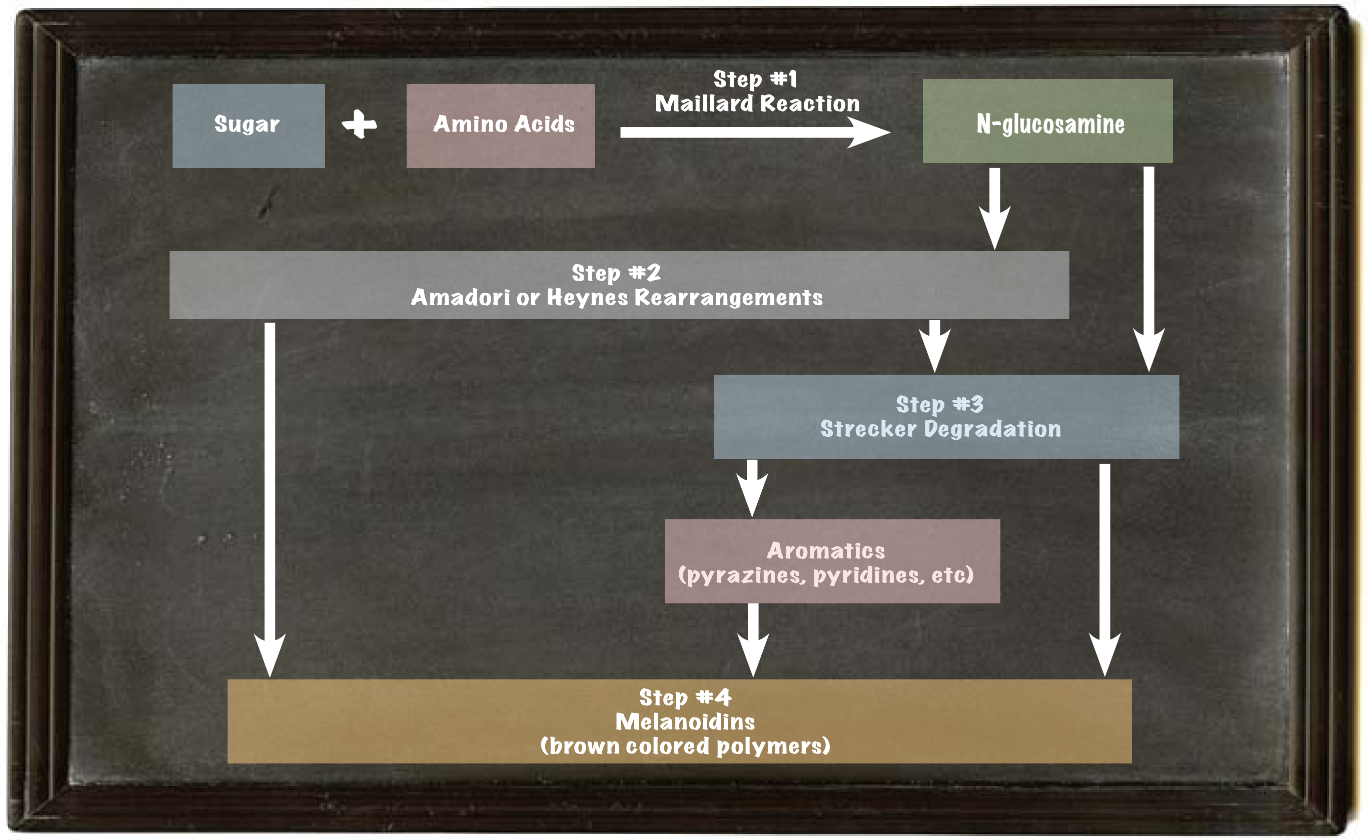
In summary, caramelization serves to create color, aroma, acids and carbon dioxide during the roasting process. Since both caramelization and the Maillard reaction (discussed next) occur at different temperatures, what we ultimately get after roasting is a product that has by-products of both.

The Maillard Reaction

Of all the reactions discussed so far, the Maillard reaction is perhaps the godfather of all browning reactions. Though the reaction is typically associated with food, its true origin is actually deeply rooted in the medical field. In 1900, Dr. Louis Camille Maillard embarked on solving one of life's most complex questions: how does the human body create proteins? His early attempts to solve this involved combining isolated amino acids in vials and agitating, with no luck. When he combined reducing sugars (glucose) and subjected the same amino acid mixture to heat, he was stunned. As heat was applied to the mixture, the solution slowly changed from a clear liquid to a brown solution, giving off nutty/bready aromas—essentially marking the discovery of the Maillard Reaction. Since then, hundreds of manufacturers have tweaked the reaction, and it now serves as a source for aroma development within the food industry. But it wasn't until after World War II—when soldiers complained that their powdered eggs were changing color and producing off-flavors—that the military seriously began to study the reaction in detail. Fifty years later, we're still unlocking the mystery of this complex reaction. Though the reaction still plays an important role in food, in recent years it's also become a topic of great interest in the medical field since it's believed to be involved in the aging process.

In essence, the Maillard reaction is the process whereby available amino acids and sugars combine in thermally processed food. We'll discuss details later, but it's essentially the reaction responsible for producing the aroma and flavor in products such as toasted bread, steak and coffee. Its been estimated that in steak and coffee alone, more than 600

continued on page 48



■ SIMPLIFIED OUTLINE OF THE MAILLARD REACTION *several detailed steps omitted for simplicity

compounds combine to create their complex aroma. And though extremely complex, what we'll discuss next is simply a layman's introduction to the Maillard reaction, as a comprehensive explanation would be outside the scope of this article.

In a nutshell, the Maillard reaction can be summarized in four major steps: In step one, amino acids combine with sugars to form several N-glucosamine compounds during roasting. Since these compounds are relatively unstable, they typically undergo a second set of reactions—Amadori or Heynes—to form several other intermediates (step two). Up until this point, all the compounds produced are colorless and lack any detectable flavor. But it's not until we reach step three, or the Strecker degradation, where a handful of N-glucosamine (those with double bonds created in step one) react with other amino acids to form compounds we typically associate with coffee aroma. Pyrazines and pyridines, which typically have maize/nutty/bitter aromas, and many other compounds are produced in this step. And finally, in step four, all remaining intermediates combine to form long chains of brown-colored melanoidins—the compound responsible for a coffee's color.

There are a number of factors that affect the Maillard reaction, including moisture level, pH and temperature. Since water is produced in the combination of amino acids with sugars, products with excess water activity actually impede the reaction. So for those products such as bread, powdered milk or powdered eggs, which already have a low water activity, browning occurs much more quickly. Also, the reaction accelerates in alkaline environments (pH greater than 7) and varies with the type of sugar and amino acid present. Though some of these factors may be out of our immediate control, the one thing we can control is temperature. According to empirical data, it's been shown that

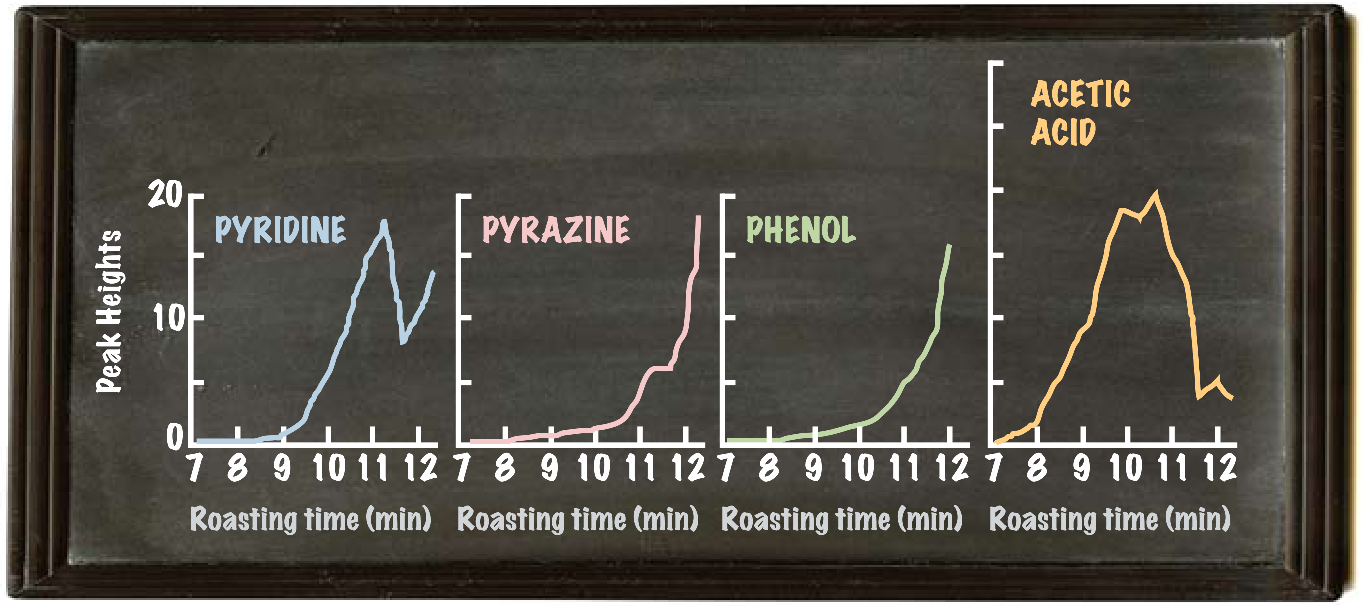
continued on page 50

Getting a Reaction

INTERESTINGLY, the Maillard reaction does not always require heat to initiate. To see one example of this, we need to go no further than our local beach. That's right, it turns out that much of the same chemistry that is involved in the Maillard reaction is actually used in the production of self-tanning creams. Though these creams don't produce a "real" tan, they do provide enough brown-colored pigment under the skin to impress a few beachgoers. Who could imagine that the same reactions that occur during coffee roasting are the same ones to occur at the beach every day, and on that stunning blonde sporting a bikini? Career change, please!

the Maillard Reaction doubles for every 10-degree increase in temperature. Interesting, but anyone who has ever taken a roast past second crack can easily attest to this. Why?

Here's the technical scoop: As the bean enters deeper roasting stages, more and more water is driven out of the bean, thereby increasing the concentration of potential reactants (much like when water evaporates in the ocean, increasing the salt concentration) and allowing more reactions to occur. Also, as temperatures elevate and changes in composition occur, several variables react to generate the flavor trends shown in the graph. We can see that as roasting progresses, a significant increase in the levels of pyrazine, phenols and pyridines is produced. Acetic acid increases in the early part of the roast, reaching a peak, then rapidly diminishing due to its volatility. There are literally hundreds of other reactions taking place simultaneously, but in the end, what does all this mean? It basically explains why we see a general increase in the level of aroma, body and astringency and a muting of acidity in darker roasted coffees.



■ GRAPH OF FLAVOR CHANGES DURING ROASTING

So at this point you're probably wondering: "Is there a difference between caramelization and the Maillard reaction? They sound similar." It's true, they do sound the same, but they aren't quite. Here's a recap:

- Caramelization does not require a nitrogen source. Remember, caramelization is simply a decomposition of sugar. This is unlike the Maillard reaction, which requires sugar and amino acid (nitrogen source).
- Caramelization occurs at much higher temperatures than the Maillard reaction. The Maillard reaction can occur at room temperature, albeit very slowly, while caramelization typically requires much higher temperatures (over 150°C).
- Both reactions form melanoidins and flavor compounds. Although caramelization and the Maillard reaction follow different paths, we essentially end up with the same type of end products—color and flavor.

Thus far, we've only skimmed the surface in attempting to explain the chemistry behind coffee roasting. Though I'm sure many people now have more questions than answers, we hope that the material presented in this month's series will serve as a good starting point for further study. In the next issue, we'll see how much of these flavor compounds created actually end up in our cup.

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Let's Review!
(we told you there'd be a quiz, didn't we?)

› What enzyme is responsible for the browning in fruits such as apples and bananas?

› What factors affect the Maillard reaction?

› What is the difference between caramelization and the Maillard reaction?