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Barbecue: The Chemistry behind Cooking on a Barbecue

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Summer is not only the time for everyone to enjoy the sun; it also gets us excited about the mouthwatering smoky taste of barbecued food. Recent data show that about 80% and 90% of American (HPBA, 2019) and French households (France Info, 2019), respectively, own barbecue grills. In Europe, the biggest barbecue fans are the Germans, followed by the French and the Polish, with 19, 17 and 17 barbecues a year, respectively (Idealo, 2019). Although these barbecue grills are mostly used during the spring and summer seasons, some people are still keen on having barbecues in the winter (75% in Italy, for instance). Although everyone agrees that charcoal- and wood-grilled food is delicious, few really appreciate the chemistry behind the great smoky flavour of barbecued meat.

Composition of Wood, Charcoal and Meat
Charcoal and wood contain three main polymer components: cellulose, hemicelluloses and lignins. While cellulose is a linear polymer made only of glucose, hemicelluloses are branched polymers constituted of various sugar residues, including residues of D-glucose, D-xylose, D-arabinose, D-galactose and D-rhamnose (Figure 11.1; Wertz et al., 2017). As these two polysaccharide components are not involved in the flavouring of the meat, their biosynthesis and precise composition will not be further discussed here.

Not only are lignins the main constituents of the cell walls in plants; they also come in second place after cellulose as the most abundant natural polymer in the world (Belitz and Grosch, 1999). Lignins are heterogeneous cross-linked polymers made of three phenolic monomers called monolignols (i.e., p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol) that differ in the degree of methoxylation on their aromatic ring. The monolignols are oxidized by enzymes such as peroxidases and laccases to provide O-centred phenoxy radicals that can then be delocalized through conjugation to lead to C-centred radical species at the 3, 1 and β positions. Finally, via radical–radical coupling, oxidized monolignols are polymerized through labile C-O-C ether bonds and strong C-C bonds, depending on the radical species involved (Figure 11.2) (Boerjan et al., 2003). Once inserted into the polymer, p-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol lead to H, G and S units, respectively. Finally, the ratio between these three monolignols in lignins depends on the plant and its environment.

When it comes to trees, hardwoods (e.g., acacia, birch, ebony, eucalyptus, maple and oak) are rich in S- and G-lignins, whereas softwoods (e.g., cedar, pine and spruce) are mainly composed of G units with traces of H units.

Meat, on the other hand, is generally composed of water (75%), proteins (19%), intramuscular fat (2.5%), sugars (1.2%) and other non-protein substances (2.3%; amino acids, minerals, etc.).

Proteins are high-molecular-weight natural polymers – polyamides – composed of amino acids that can be modified through thermally or enzymatically induced hydrolysis (Figure 11.3).

Flavour from the Burning Wood
When wood and charcoal burn, cellulose, hemicelluloses and lignins are thermally degraded. Lignins are responsible for the smoky flavour; indeed, a variety of phenolic compounds are generated through the oxidative degradation of lignins via pyrolysis. Among these phenolics, the most important are two ortho-methoxy phenols, guaiacol and syringol, that cause the smoky taste and the smoky smell, respectively. When present in the smoke, these two phenolics are entrapped by the moisture of the grilled food and infuse it.

Also known as 3-methoxyphenol (CAS 90-05-1, C₇H₈O₂), and first isolated by O. Unverdorben in 1826 (Stevens et al., 1943), guaiacol is one of the main components of the smoke generated when wood,charcoal burns (Figure 11.4). It is noteworthy to mention that guaiacol is naturally present in plants such as Guaiacum and can be biosynthesized by certain organisms (Duffey and Blum, 1977). Guaiacol is also found in whiskey and roast coffee, and is commonly used to produce vanillin at the industrial level.

Similarly to guaiacol, syringol (2,6-dimethoxyphenol, CAS 91-10-1, C₈H₁₀O₃) is also found in wood,charcoal smoke and is
produced through the pyrolysis of lignins (Figure 11.4). Synthetic syringol is commonly used as smoke flavouring for those who want the barbecue taste without having to grill the food (this also avoids consumption of benzopyrenes).

Although the mechanisms of the formation of guaiacol and syringol through the pyrolysis of lignins are still rather unclear, homolytic breakage of the Cβ-O and the Cα-C1 bonds in lignins is necessary (Figure 11.5). It is noteworthy that, as guaiacol and syringol are derived from G and S units, respectively, the guaiacol/syringol ratio in the smoke therefore depends strongly on the wood species used for the barbecue.

**Flavour from the Cooked Food**

Wood and charcoal have been proven to play a crucial role in the production of the smoky taste and smell; however, the glycation reactions sometimes called Maillard reactions also strongly contribute to the delicious flavour of grilled food. Moreover, these also provide the grilled meat with the characteristic brown colour.

Discovered by Louis Camille Maillard in 1912 (Everts, 2012), these reactions involve the amino acids (obtained through the breakdown of the proteins) and the reducing sugars present in the meat. Similarly to the mechanisms of formation of guaiacol and syringol, that of Maillard products remains unclear.

However, it is generally accepted that the Maillard reaction proceeds as shown in Figure 11.6. The reducing end of the sugars reacts with the amine moiety of the amino acids to form an imine (called a Schiff base). The latter undergoes an isomerization to provide the enol, which is in equilibrium with the corresponding ketone (1,2-enolization) that is also known as the Amadori product. Through a combination of reactions such as deamination, dehydration and fragmentation, the Amadori products can then lead to a very complex mixture of a wide variety of products (e.g., furans, thiophenes, furanones, alkyl- and acylpyridines, pyrazines, pyroles and oxazoles), each having its own type of taste and odour (Figure 11.7).

Melanoidins, polymers also produced through the Maillard reactions, contribute to the colouration of the grilled food. As this reaction only occurs at temperatures above 110 °C, the browning is mainly observed on the surface of the meat.

Due to the composition of amino acids and sugars being quite different from one kind of meat to another, the large diversity brought by the Maillard reaction therefore leads to a wide range of different flavour profiles.

**Harmful Substances Created through Barbecuing**

Although wood- and charcoal-grilling brings delicious smoky flavour and smell to the meat, it can also generate harmful chemicals. The most common ones are polyaromatic hydrocarbons (PAH), the heterocyclic amines (HCA) and acrylamide.

PAH are formed when melted fat drips on hot charcoal, and some are proven carcinogens, such as benzo[a]pyrene (Figure 11.8) (Phillips, 1999). Production of PAH by cooking over charcoal, being a function of both the fat content of the meat and the proximity of the meat to the heat source, can be reduced by cooking for longer periods at lower temperatures.

HCA and acrylamide are intimately linked to the Maillard reaction. Indeed, HCA are formed as meat cooks and are
FIGURE 11.2 Lignin biosynthesis.
FIGURE 11.3  General structure of proteins.

FIGURE 11.4  Guaiacol and syringol.

FIGURE 11.5  Guaiacol and syringol formation via lignin pyrolysis.
FIGURE 11.6  Maillard reaction and related products.  
(Halford et al., 2012)
generally found in the charred parts of the cooked meat. These compounds result from the reaction of creatine with other amino acids and monosaccharide-derived aldehydes at temperatures between 125 °C and 300 °C (Figure 11.9) (Skog et al., 1998). It is noteworthy that such compounds can be obtained at lower temperatures with longer cooking time. Low-fat meats have been shown to generate less HCA (Jägerstadt et al., 1998). Just like PAH, these compounds are also carcinogenic.

Acrylamide, which has been identified as one of the many compounds that can be obtained through the Maillard reaction (Figure 11.10) (Mottram et al., 2002), is another potential carcinogen. Although high doses of acrylamide cause cancer in mice and rats, considering the relatively low concentration of acrylamide in consumed grilled meat, the risk associated with barbecuing remains quite low as long as the meat is not cooked at too high a temperature for excessive times.

**Conclusion**

If it were not for lignin pyrolysis and the Maillard reaction, we would not enjoy delicious grilled meats with their burst of flavours and brown colours. Phenols, sugars and amino acids are responsible for this popular cooking style, that is, barbecue grilling. Although grilling meat over wood or charcoal seems to be the easiest – if not the oldest – way humans cook food, the chemistry that hides behind it is quite complex. Indeed, there are various parameters that come into play, not only at the flavour
level but also in terms of potential toxicity. For instance, wood and charcoal origins (i.e., tree type) will significantly impact the overall flavour, whereas the cooking duration and temperature, as well as the distance between the meat and the fire, can both be tuned to limit the production of toxic compounds such as PAH, HCA and acrylamide. With so many parameters (e.g., meat type, wood charcoal, temperature and cooking duration), almost an infinite number of recipes can be created. Finding the ones that will fit what your taste buds crave is just a matter of experimentation. Who knew that barbecuing is so reliant on chemistry?

REFERENCES


FIGURE 11.9 Suggested pathway of HCA formation.
(Jägerstadt et al., 1998)

FIGURE 11.10 Production of acrylamide.


