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The formation of polycyclic hydrocarbons during smoking process of cheese

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Summary

The smoking process determines the characteristic flavour, odour, colour and texture of several cheese varieties. Some smoke compounds are known to have bacteriostatic and antioxidant effects, and may act as preservatives. Smoked cheese is appreciated by consumers due to its sensorial properties. However, with smoking process there is a risk of formation of toxic polycyclic aromatic hydrocarbons (PAHs). This review emphasises the occurrence of polycyclic hydrocarbons on smoked cheeses and their health impacts.

Key words: cheese, smoking process, polycyclic hydrocarbons

Introduction

The smoking of foods is one of the oldest methods of preservation. However, foods are nowadays smoked for sensory quality rather than for the preservative effect. Sensory characteristics are one of the important quality attributes that a consumer uses to judge the acceptability of a product. Colours of smoked cheese available in the market range from golden yellow to dark brown, and this array of colouration suggests that producers of smoked cheese have different opinions concerning consumer preferences. Similar to colour cheese flavour is diversified by smoking (Möhler 1980; Asita et al., 1990; Müller 1991; Riha and Wendorff, 1993; Rehman et al., 2003; Ozcan et al., 2008).

In the analysis of smoked cheese with headspace-solid phase extraction method a broad range of compounds, such as acids, alcohols, esters, hydrocarbons, aldehydes, ketones, furan and pyran derivatives, terpenes and sesquiterpenes as well as ethers, of diverse volatility, molecular weights and nature were determined (Guillen and Sopelana, 2005).

Polycyclic aromatic hydrocarbons (PAHs), that are composed of two or more fused aromatic rings (EC, 2002; EFSA, 2008) and having a strong lipophilic character (Simko, 2005), constitute a widespread group of contaminants (Guillen et al., 1997). PAHs are formed by incomplete combustion or pyrolysis of organic material. With traditional smoking process applied to any food material, in which food and the smoke comes in direct contact, toxic PAHs are formed. Temperature, humidity, type of wood/coal, oxygen concentration during smoke generation, and the type of smoke generators are effective on formation of possible PAHs (Toth and Potthast, 1984; Chiu et al., 1997; Ozcan et al., 2008; Duedahl-Olesen et al., 2010).

It is worth to mention that some PAHs are able to interact with organisms through enzymes (such as aryl hydrocarbon hydroxylases) to form PAH dihydrodiol derivatives. These reactive products are able to form covalent bounds with proteins and nucleic acids which typify them as carcinogens. In general, the alterations of DNA expressions are thought to be involved in cell mutation which results malig-

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nancy (IARC, 1987; Stahl and Eisenbrand, 1988; Bartle, 1991; Rogan et al., 1993). The most potential mutagenicity due to smoking was observed in PAH fractions isolated from smoked fish, treated before smoking with nitrites in an acid solution (Kangsadalampai et al., 1997).

Polycyclic aromatic hydrocarbons in smoked cheese

The presences of PAHs in foods have been ascribed mainly to smoking, drying, roasting, cooking and barbecuing processes (Guillen et al., 1997; Philips, 1999; Guillen et al., 2000; EC, 2002; Duedahl-Olesen et al., 2006).

Studies have referred that cereals, fats, oils, and derived products are the main responsible foods for the daily intake of PAHs (Dennis et al., 1983; De Vos et al., 1986; Lodovici et al., 1995). Aside these products, smoked foods are suspected of containing considerable amounts of PAHs (Fretheim, 1976; Joe et al., 1984; Larsson et al., 1988; Gomma et al, 1993; Karl and Leinemann, 1996).

The smoke, produced by either cold/hot smoking or liquid smoking, contributes to formation of the characteristic flavour, odour, colour and texture (Bratzleretal et al., 1969; Gilbert and Knowless, 1975; Möhler 1980; Poulter, 1988; Horner, 1992; Riha and Wendorff, 1993; Wendorff et al., 1993; Atasever et al., 1999; 2003). The smoking process itself is based on successive deposition of compounds, such as phenol derivates, carbonyls, organic acids and their esters, lactones, pyrazines, pyrols, and furan derivates on a food surface with their subsequent migration into a food body (Maga, 1987; Simko et al., 1991). Smoke is a polydisperse mixture of liquid and solid components in the gaseous phase of air, carbon oxide, carbon dioxide, water vapour, methane, and other gases, which are developed by combustion of cellulose, hemicelluloses, and lignin, with limited access of oxygen. Thermal combustion of these pyrolysis products proceeds at 180-300, 260-350, and 300-500 °C, respectively. However, decomposition of wood components occurs also at temperatures up to 900 °C (Simko, 2005; Terzi and Celik, 2006).

It has been well documented that smoke generation conditions can dramatically influence the level of resulting PAHs in the smoke and, consequently, in smoked foods (Gilbert and Knowles, 1975; Maga, 1988). Chen and Lin (1997) compared the PAH amounts in different cooking methods and reported that the highest amount of PAH occurred in flame cooking and the lowest PAH occurred in liquid smoking.

Maga (1988) stated that moistening the wood during smoking gives rise to smoke with lower PAH concentrations than dry woods, because it lowers the smoke generation temperature.

Another factor considered to be related to the production of PAHs is wood nature. The use of hardwoods instead of softwoods has been recommended to reduce the presence of PAHs in smoke and in smoked foods (Maga, 1988). However, there are not many studies which show the influence of this factor on the level of PAHs in the smoke, and they are conflicting. Results obtained by Potthast (1979) showed that the PAH concentrations found in smoke coming both from softwood (pine) and hardwood (beech) are very similar. However, another study on PAHs in fish smoked using different woods (Larsson, 1982) revealed that softwoods had a slight tendency to produce higher concentrations of heavy PAHs.

Guillen et al. (2000), studied the influence of wood nature on the PAH content of smoke flavourings. They obtained five liquid smoke flavourings from dry sawdust of different sources of wood, and found that the flavouring from poplar wood presented the highest number and concentrations of both total and carcinogenic PAH. Even though, the occurrence of PHAs in smoked cheese has not been studied extensively, considering the high solubility of PHAs in lipids and the high proportion of fat in cheese, these contaminants can easily retain during the smoking process (Joe et al., 1984; Riha et al., 1992; Guillen and Sopelana, 2004).

Cheese is an essential dairy product in human nutrition for centuries that can be consumed either fresh or matured. It is manufactured by draining the whey after coagulation of casein in milk by addition of either coagulating enzymes or food-grade acidulants (Fox, 1993). As in the manufacture of other commodities, smoking is an option in cheese making (Wasilevski and Kozlowski, 1977; Ulyanov et al., 1979; Mcllveen and Vallely, 1996; Atasever et al., 1999; 2003; Rajbhandari and Kindstedt,

2005). There are well-known smoked cheese varieties much appreciated for their special organoleptic properties, such as Apple wood, Gruyere as well as Gouda, Cheddar, Lancashire, Stilton, Brie, Rauchkase and Scamorza.

Most of the studies on the occurrence of PHAs in smoked cheese mainly refer only to benzo[a] pyrene (Lijinski and Shubik, 1965; Howard et al., 1966; Crosby et al., 1981; Phillips 1983; Joe et al., 1984; Riha et al., 1992; Potthast, 1977; Garcia-Falcon et al., 1999). Benzo[a]pyrene ($C_{20}H_{12}$; BaP) is a five-ring PAH which is an effective mutagen and carcinogen, and is the most often determined compound as a surrogate for all PAHs. Animal studies have shown that dietary intake of BaP causes increased levels of tumours at several sites, particularly in the upper gastrointestinal tract. In these studies animals are exposed to BaP with subcutaneous injection, and digestion system, tumours observed in carcinomas of lung and local sarcomas (Kazerouni et al., 2001). There is not enough epidemiological studies with acute and subchronic effects of BaP, however genetic, chronic and carcinogenic effects of BaP to humans (IARC, 1987; ASTDR, 1995).

It must be mentioned that there is no clear pattern in the concentrations of PHAs found in cheese by the researchers. It is observed that the most abundant PAHs are benzo[a]pyrene, phenanthrene, fluoranthene, anthracene, pyrene, chrysene, coronene, and naphthalene (Fig. 1). Guillen and Sopelana (2004), detected over 320 components in smoked artesian cheese of different origin. They have found various acids and phenolic derivatives aside with a high number of PAHs of differing molecular weights as main flavour components. Also, they mentioned that the levels of benzo[a]pyrene ranged from non-detected to 0.91 μg/kg. The researchers have found both compounds of low molecular weight (naphthalene, acenaphthene, fluorene) and of high molecular weight (benz[a]pyrene, benzo[a]pyrene, benzo[g,h,i]perylene), even though compounds of 2,3- and 4- aromatic rings draw the attention.

On the other hand, among the studies including a higher number of PAHs, some of them do not clearly state whether they are on smoked or unsmoked cheese (Dennis et al., 1991; Lodovici et al., 1995). The differences among the results of different researchers could be attributed to the contamination source of the cheese samples or to the used chromatographic method and detection systems.

Legal restrictions and toxicological effects of PAHs

In the past decade PAHs were evaluated by the International Programme on Chemical Safety (IPCS), the Scientific Committee on Food (SCF) and by the Joint FAO/WHO Expert Committee on Food Additives (JECFA). SCF concluded that 15 PAHs, namely benz[a]anthracene, benzo[b] fluoranthene, benzo[j]fluoranthene, benzo[k] fluoranthene, benzo[g,h,i]perylene, benzo[a]pyrene, chrysene, cyclopenta[c,d]pyrene, dibenz[a,h]

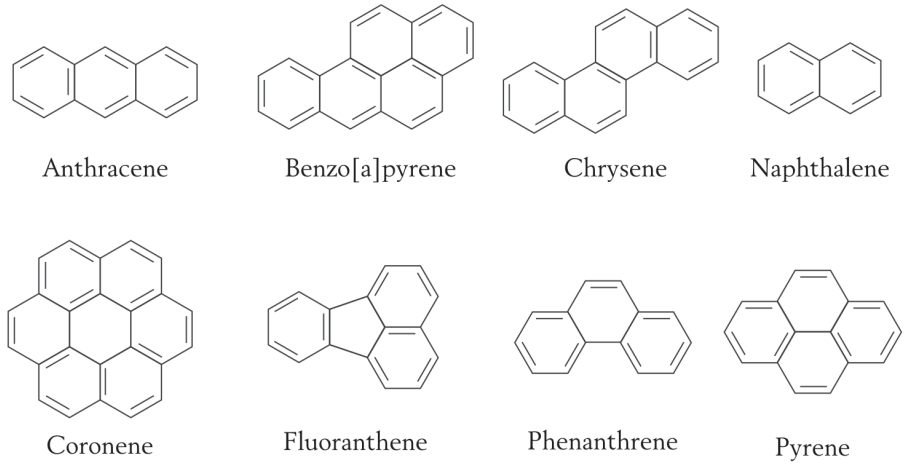

Figure 1. Structure of some PAHs detected in smoked cheese

anthracene, dibenzo[a,e]pyrene, dibenzo[a,h] pyrene, dibenzo[a,i]pyrene, dibenzo[a,l]pyrene, indeno[1,2,3-cd]pyrene and 5-methylchrysene may be regarded as potentially genotoxic and carcinogenic to humans and, therefore, represent a priority group in the assessment of the risk of long-term adverse health effects following dietary intake of PAHs. SCF suggested using benzo[a]pyrene as a marker of occurrence and effect of the carcinogenic PAHs in food, based on examinations of PAH profiles in food and on evaluation of a carcinogenicity studies in animals (World Health Organization, 1991; 1998; IPCS, 1998; Terzi and Çelik, 2006; EFSA, 2008).

Some of the PAHs identified in commercial smoked cheese samples such as benzo[b,j,k] fluoranthenes or indene[1,2,3-cd]pyrene, have been considered by the IARC as "possibly carcinogenic to humans (group 2B)" and others as "probably carcinogenic to humans (group 2A)"; among these latter benz[a]anthracene, benzo[a]pyrene, and dibenz[a,h] anthracene can be cited (IARC, 1973; 1983; Guillen et al., 2007).

In Germany, the maximum acceptable limit of benzo[a]pyrene has been set as 1 μg/kg in smoked meat since 1973. In many European Countries the same limits are accepted. EU reported in EEC Directive 88/388 (EEC, 1988) that the acceptable limit of benzo[a]pyrene is 10 μg/kg, and also the Turkish Food Codex (2008) declare the limits as 0.01 μg/kg in marine products and 0.001 μg/kg in meat products. However, there are no regulations about smoked cheese and their maximum PAH concentrations (Terzi and Celik, 2006).

Conclusion

The control of PAHs in the human food chain is essential due to the mutagenic and carcinogenic potential of these compounds. Smoked cheese is a popular food, but to our knowledge, there are only several papers that focus on PAH levels in cheese. Given that smoking differentiates organoleptic properties that are much appreciated by consumers, attention must be paid to smoking time, combustion temperatures, and smoke-generating material in order to reduce formation of PAHs in cheeses. For this purpose, the process must be carefully controlled in terms of pyrolysis. It is mentioned that combustion temperature should be lower than 300°C to minimize the risk of PAH formation. Also in order to avoid PAH in cheese the liquid smoke atomization process can be an alternative to traditional smoking process.

Formiranje policikličkih ugljikohidrata tijekom procesa dimljenja sira

Sažetak

Dimljenje određuje specifičnost arome, mirisa, boje i tekstura nekim vrstama sira. Poznata su bakteriostatska i antioksidativna svojstva za neke spojeve dima, te mnogi među tim spojevima imaju konzervirajući učinak. Dimljeni su sirevi cijenjeni među konzumentima zbog svojih senzorskih osobina. Međutim, postupkom dimljenja postoji određeni rizik za nastajanje otrovnih policikličkih aromatskih ugljikohidrata (PAU). Ovaj pregledni članak naglašava pojavu policikličkih ugljikohidrata u sirevima i njihov utjecaj na zdravlje konzumenata.

Ključne riječi: sir, dimljenje, policiklički ugljikohidrati

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