Smoking out carcinogens

Dave Baines, Huw Griffiths and Jane Parker introduce a ground-breaking, new smoke filtration technology which can significantly reduce the presence of carcinogens in aerosol smoke used to produce smoked food products.

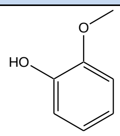
Smoked foods are becoming increasingly popular and are being produced by large and small food operations, artisan producers, chefs and consumers themselves. Epidemiological studies conducted over a number of decades have linked the consumption of smoked foods with various cancers and these findings have been supported by animal testing. Smoke contains a group of dangerous carcinogens that are responsible for lung cancer in cigarette smokers and implicated as causative agents for colorectal and other human cancers resulting from the consumption of smoked and barbequed food products. This article describes a new innovation in smoke filtration technology that can significantly reduce the presence of carcinogens in aerosol smoke used to produce smoked food products and hence largely remove a group of dangerous chemicals from the food supply.

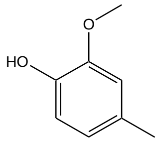
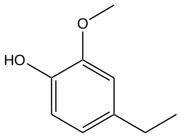
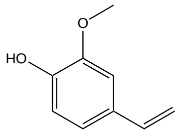
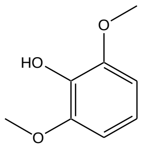
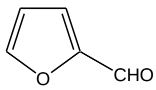
The flavour of smoke

Smoking is the age-old process of preserving food. Smoke derived from the burning of wood adds flavour and colour, changes texture through dehydration and reduces surface bacteria extending the shelf-life of the food product. Meat and fish are typically smoked but cheeses, vegetables, spices and other foods can also be smoked. Phenolic compounds in smoke derived from the burning of the lignin fraction of wood act as natural preservatives but also add their own distinctive flavour character blending with the flavour of the base food to create a taste that is appreciated for its quality and uniqueness. Some foods lend themselves well to the smoking process and smoked haddock, hot and cold smoked salmon and smoked bacon immediately spring to mind.

Different woods add their own distinctive flavour characteristics the most popular being beech, oak, hickory, maple and mesquite. The compounds responsible for the flavour of smoke have been studied by a number of workers; the phenols are the predominant character impact compounds tempered by short chain fatty acids, ketones, diketones and furans. Table 1 shows the organoleptic profile of the main smoke compounds and their contribution to smoke flavour expressed by their 'odour activity values' (OAVs). The OAV is calculated as the ratio between the concentration of individual substances in a sample and the threshold concentration of the substance (minimum concentration that can be detected by the human nose). Where quantitative data is lacking, relative OAVs can still be used as an indication of the contribution of volatile compounds to the flavour.The higher the relative OAV, the greater the contribution of the substance to the flavour of smoke.

Table 1 Organoleptic profile of the main smoke compounds in smoked water

NAME	STRUCTURE	ORGANOLEPTIC PROFILE	THRESHOLD[1] µg/L (ppb)	Relative OAV
Guaiacol		Odour: phenolic, smoke, spice, vanilla, woody, medicinal. Taste: Woody, phenolic, bacon, savoury, smoky, medicinal (2ppm).	Odour: 3-21 ppb (in water)	76,000
4-Methyl guaiacol		Odour: spice, clove, vanilla, phenolic, medicinal, leather (10%	Odour: 21 ppb (in water)	10,000

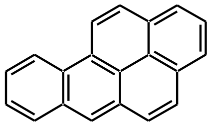
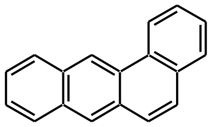
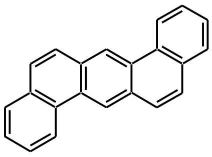
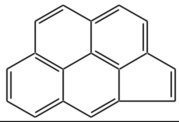
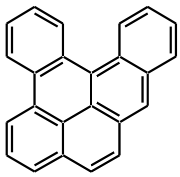
		in PG). Odour: Sweet, candy, spice, eugenol, vanilla, leather, spicy, smoky (1% in ethanol) Taste: vanilla, spice, eugenol, woody and leather nuances with no residual chemical notes (10ppm).		
4-Ethyl guaiacol		Odour: spicy, smoky, bacon, phenolic, clove, medicinal, woody with sweet vanilla nuances. Taste: woody, smoky, spicy with sweet vanilla background.	Odour: 50 ppb (in water)	1,240
4-Vinyl guaiacol		Odour: dry, woody, fresh amber, cedar, roasted peanut. Taste: smoky bacon.	Odour: 3 ppb (in water)	2,400
Syringol		Odour: smoky, phenolic, balsamic, bacon, powdery, woody (1% in PG) Odour: sweet, phenol, smoky, medicinal, balsamic. Taste: sweet, medicinal, creamy, meaty, vanilla, spice (60ppm).	Odour: 1850 ppb (in water)	10
Furfural		Odour: sweet, woody, almond, fragrant baked bread (1% in PG) Odour: sweet, brown, woody, bready, caramelic with slight phenolic nuance. Taste: brown, sweet, woody, bready, nutty, caramellic with a burnt astringent nuance (30ppm)	Odour: 3000-23000ppm (in water) Flavour/taste: 5000ppb (in water)	1,720

By far the largest contribution to smoke flavour is from guaiacol, which possesses a phenolic, smoky character. Other phenols make a contribution, and furfural and other sugar degradation products may add a more fragrant woody, caramellic character. Other compounds may play minor roles and the flavour of smoke may also be influenced by the PAHs, which collectively could play a role in the taste and organoleptic character but, because of the extreme hazard, thresholds will never be measured for this group of compounds.

The problem with smoke - polycyclic aromatic hydrocarbons

The polycyclic aromatic hydrocarbon (PAH) benzo[a]pyrene (2) is classified as a Group 1 carcinogen by the IARC. Group 1 means that it is a proven human carcinogen and one of the most dangerous chemicals occurring in food. It is responsible for lung cancer in smokers and epidemiological and experimental studies have established that it is also responsible for a range of cancers in humans as a result of the consumption of smoked food products including processed meats. It is just one of a number of polycyclic aromatic hydrocarbons produced in the generation of smoke. It is highly likely that many of the other PAHs are equally as lethal in terms of carcinogenicity but they have not been studied to the extent of benzo[a]pyrene (Table 2).

Table 2 Compounds in smoke that are known carcinogens or probable carcinogens to humans

Benzo[a]pyrene	Group 1 Known animal carcinogen	IARC ATSDR	
Benz[a]anthracene	Group 2A Known animal carcinogen	IARC ATSDR	
Dibenz[a,h]anthracene	Group 2A Known animal carcinogen	IARC ATSDR	
Cyclopenta[c,d]pyrene	Group 2A	IARC	
Dibenzo[*a,l*]pyrene	Group 2A	IARC	

IARC: International Agency for Research on Cancer. ATSDR: Agency for Toxic Substances and Disease Registry. GROUP 1 = Carcinogenic to humans GROUP 2A = Probably carcinogenic to humans.

PAHs are formed through the pyrolysis of wood during the smoking process but also when fat in juices from meat grilled directly over an open fire drip onto the fire causing flames. These flames contain PAHs that adhere to the surface of the meat.

The flavour industry has developed smoke flavourings by condensing aerosol smoke in water then subjecting this solution to a purification process. The smoke flavourings produced can be painted onto or injected into food products or mixed with food ingredients in products, such as sauces and marinades. The invention of smoke flavourings was an innovation that enabled the application of smoke across the food chain and into products that previously had not been traditionally smoked. As a consequence this spread the carcinogens across a wider range of food groups.

The European Union initiated an evaluation of smoke flavourings (smoke condensates) used in food products in the EU to determine the risk to consumers and to approve a list of permitted smoke flavourings and their maximum levels of use. The Regulations covering this are 1334/2008, 2065/2003 and 1321/2013. The latter Regulation lists the smoke flavourings and the levels of use that are now permitted in the EU (Table 3).

Table 3 Smoke flavourings permitted in the EU

SMOKE PRODUCT	COMPANY	COUNTRY	SOURCE MATERIALS
Tradismoke A Max	Nactis	France	Beech
proFagus-Smoke R709	ProFagus	Germany	90% Beech, 10% Oak
Scansmoke PB 1110	Azelis	Denmark	90% Beech, 10% Oak
Scansmoke SEF 7525	Azelis	Denmark	35% Red Oak, 35% White Oak, 10% Maple, 10% Beech, 10% Hickory
SmokeEz C-10	Kerry (Red Arrow)	Germany/ USA	25-60% Maple, 10-40% Oak, 10-25% Hickory
SmokeEz Enviro 23	Kerry(Red Arrow)	Germany/ USA	25-65% Maple, 20-75% Oak, 0-15% Hickory, Ash, Birch, Cherry, Beech.
Fumokomp	Kompozicio KFT	Hungary	85% Beech, 15% Hornbeam.
Zesti Smoke Code 10	Mastertaste Kerry	United Kingdom	50-60% Hickory, 40-50% Oak
AM 01	Aromarco s.r.o.	Slovak Republik	Beech
Smoke Concentrate 809045	Symrise AG	Germany	Beech

Recital 6 of 2065/2003 states *'Because smoke flavourings are produced from smoke which is subjected to fractionation and purification processes, the use of smoke flavourings is generally considered to be of less health concern than the traditional smoking process'*. This leaves one wondering about the safety of smoked foods where there are no stringent controls as there are with smoke flavourings and where smoking food is a process undertaken by large and small companies, artisan producers and by consumers themselves. There is no doubt that the consumption of smoked foods is responsible for human cancers. Research has shown that high consumption of well-done, fried or barbecued meats was associated with increased risks of colorectal, pancreatic and prostate cancers[2].

Smoked food legislation

The legislation covering smoked food products is not as robust as that covering smoke flavourings. The EU has set maximum levels of PAHs in foodstuffs via Regulation (EC) No 1881/2006 amended by Regulation (EU) No 835/2001. Recently the EU published Regulation (EU) No2015/1933 in regard to maximum levels of PAHs in cocoa fibre, banana chips, food supplements, dried herbs, dried spices. Indent 7 of this Regulation *states 'Traditional smoking and processing methods applied to smoked paprika and cardamom result in high levels of PAHs. Given that the consumption of these spices is low and to enable these smoked products to remain on the market, it is appropriate to exempt these spices from the maximum levels.'* This really emphasises the point that there is little control over the incidence of PAHs in food products. Testing is only done as part of commissioned surveys and there are few, if any, routine quality control tests undertaken to check the PAH levels of smoked foods sold to the general public. It would seem that considering the traditional and cultural importance of food smoking, the EU is reluctant to enforce legislation in the way that it has done for smoke flavourings.

PureSmoke™ Filtration Technology

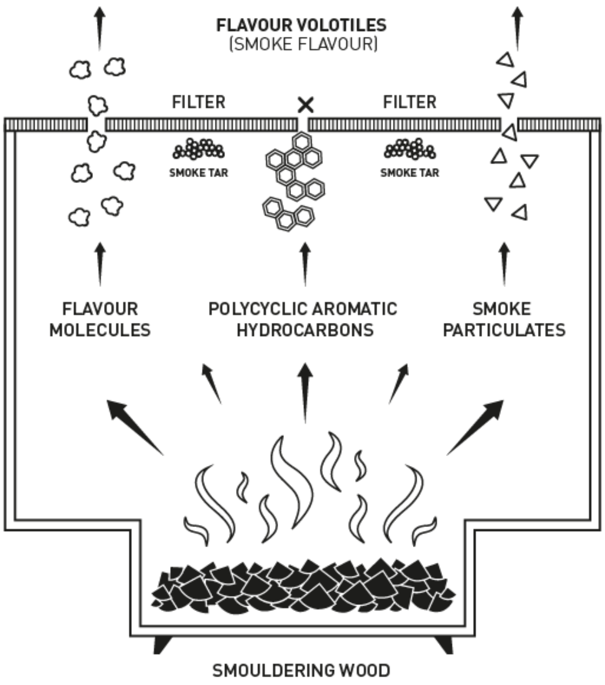
A new approach was needed to combat the presence of PAHs in the food supply. The structural size difference between the compounds responsible for the flavour of smoke (Table 1) and the PAHs (Table 2) offers potential for separating these compounds. In 2013 a small team from the University of Reading Flavour Centre and the company Besmoke secured a SPARK grant to evaluate the feasibility of using size exclusion technology to remove or significantly reduce the levels of PAHs in aerosol smoke without affecting the presence of the desirable flavour compounds present. The active agent used in the work was a natural zeolite, which is a crystalline alumina-silicate lattice linked by oxygen atoms to form a stable cage-like framework. Each aluminium atom introduces one negative charge on the tetrahedral framework, which is balanced by an exchangeable cation. The interesting feature of this material is that the cavities throughout the structure allow it to behave like a molecular sieve, preventing the passage of the larger, undesirable PAHs and facilitating the flow of the smaller flavour molecules.

The structure of the zeolite was physically and chemically modified to optimise the sieve filtration properties required to trap PAHs but allow the free flow of flavour compounds. Powder diffraction X-ray analysis (PDXRA) carried out at Reading University was used to determine zeolite structure before and after modifications.

Laboratory trials were initiated to evaluate the performance of the treated zeolite; smoke samples were analysed for flavour compounds by Gas Chromatography/Mass Spectrometry (GC/MS) at the University of Reading Flavour Centre and for PAH concentrations using GC/MS at a UKAS accredited independent laboratory. When a control smoke was compared with a smoke passed through a bed of treated zeolite, a 94.5% overall reduction in the most harmful PAHs with four rings or more (in other words the carcinogens listed in Table 2) was demonstrated.

The successful outcome of this early stage project led to a further grant from Innovate UK and the development and patenting of a new smoke filtration technology, known as

PureSmoke™, which uses molecular size exclusion to prevent undesirable elements of the smoke reaching the food.



The real test came with a tasting experiment where a comparison was made of two samples of smoked tomato sauce, one treated with regular smoke and the second treated with smoke treated with PureSmoke™ Technology. Flavour analysis was conducted with expert and consumer sensory panels at the University of Reading, comparing foods smoked with and without PureSmoke™. The taste of the tomato sauce with the treated smoke was judged to be sweeter and more balanced than the untreated sample because it had lost some of the harsh, acrid notes of smoke and the oiliness on the palate. No-one has ever tasted PAHs but the difference could be the result of their removal.

For the first time ever it is possible to reduce the exposure of consumers to a group of dangerous carcinogens in the food supply. The current target for commercially manufactured smoked foods using PureSmoke is a reduction of 85% of the most harmful PAHs, although the aim is to reach a 90%-95% reduction by 2017.

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