Plenary paper

SMOKED MEAT PRODUCTS - INNOVATIVE STRATEGIES FOR REDUCTION OF POLYCYCLIC AROMATIC HYDROCARBONS BY OPTIMISATION OF THE SMOKING PROCESS

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Abstract – The contents of polycyclic aromatic hydrocarbons (PAH) in Frankfurter-type sausages were investigated in depency on hot smoking conditions (glow smoke), type of casing, back fat content and different types of wood chips. For the smoking experiments three different types of smoke densities and ventilator velocities, three types of casings, four different back fat contents (10%, 20%, 30%, and 39%) and ten different types of wood chips were used. The smoking conditions had influence on the smoke generation temperature and the formation of PAH. The PAH contents increased with smoke density and ventilator velocity. Also the type of casing and the back fat content of Frankfurter-type sausages had an influence on the PAH contents. The use of poplar and hickory wood chips led to a decrease in the PAH contents compared to the commonly used beech wood.

Key words – strategies, reduced, PAH, smoking process.

I. INTRODUCTION

Smoking is one of the oldest technologies for the conservation of meat and meat products, and is defined as the process of penetrating meat products with volatiles resulting from the thermal destruction of wood [1]. As a desired consequence of smoking, phenolic substances are generated, which are of considerable importance for the organoleptic properties of smoked meat products and show antimicrobial as well as antioxidative properties.
However, as an undesired consequence of smoking, polycyclic aromatic hydrocarbons (PAH) are generated due to the incomplete combustion of wood. About 660 different compounds belong to the PAH group, some thereof show carcinogenic properties [2]. Due to the carcinogenic properties the PAH contents in food should be ‘‘as low as reasonably achievable’’ [3].

In the European Union two maximum levels for PAH in smoked meat products are existing: A maximum level for benzo[a]pyrene (BaP) (5 µg/kg) and a maximum level for the sum content of the four PAH compounds BaP, chrysene (CHR), benzo[a]anthracene (BaA), and benzo[b]fluoranthene (BbF) (PAH4) of 30 µg/kg. In September 2014 these maximum levels will be lowered to 2 µg/kg (BaP) and 12 µg/kg (PAH4), respectively (Commission Regulation (EC) No 1881/2006 amended by Commission Regulation (EU) No 835/2011) [6].

The main objective of the studies was to analyse correlations between the PAH contents (BaP and PAH4) and the glow smoke conditions (different types of smoke densities and ventilator velocities), the type of casing (collagen casing, cellulose-peelable casing, and sheep casing), the back fat contents (10%, 20%, 30%, and 39%) and the used type of wood (oak, poplar, hickory, spruce, fir, alder, beech, and beech with apple-smoking spice mix, cherry-smoking spice mix, and a mix of juniper berries and bay leaves). The smoking experiments were performed, until comparable smoking colours were obtained.

II. MATERIALS AND METHODS

Preparation of Frankfurter-type sausages

The basic formulations as well as the applied casings for all smoking experiments are shown in Table 1.

Table 1 Basic formulations and used casings of Frankfurter-type sausages for the different smoking experiments

Experiment	pork (%)	beef (%)	back fat (%)	ice (%)	casing
(A) different smoking conditions					
A1-A24	29.4	19.6	26.5	22.5	sheep
(B) casing types					
B1	29.4	19.6	26.5	22.5	cellulose
B2	29.4	19.6	26.5	22.5	sheep
B3	29.4	19.6	26.5	22.5	collagen
(C) fat contents					
10% fat	35.8	23.9	9.9	28.3	sheep
20% fat	32.0	21.3	19.6	25.0	sheep
30% fat	28.0	18.7	29.5	21.8	sheep
39% fat	24.1	16.1	39.1	18.7	sheep
(D) Types of wood					
D1-D10	29.6	19.8	25.9	22.6	sheep

For the smoking experiments applying different smoking conditions (A), types of casings (B), and types of wood (D) identical formulations were used. For experiment B1 cellulose casings (20-22 mm), for B2 sheep casings (18-20 mm), and for B3 collagen casings (20-22 mm) were used. The smoking experiments (C) with different fat contents (10%, 20%, 30%, and 39%) were performed with Frankfurter-type sausages containing different portions of fresh pork, fresh beef, back fat, and crushed ice.

Smoking experiments

For the smoking experiments (Table 2) a T1900 smoking chamber with a smouldering smoke generator (RZ 325) obtained from Fessmann (Winnenden, Germany) was used.

Table 2 Different process parameters of the smoking experiments

Experiment	Smoking time (min)	Smoke density	Ventilator velocity (rpm)	Additional information
(A) Different smoking conditions (48 samples, 48 smoking experiments)				
A1a,b	12	Intensive	3000	Moisture of wood 12.0 %
A2a,b	11	Intensive	1500	Moisture of wood 12.6 %
A3a,b	10	Intensive	750	Moisture of wood 12.1 %
A4a,b	22	medium	3000	Moisture of wood 13.0 %
A5a,b	21	medium	1500	Moisture of wood 12.9 %
A6a,b	20	medium	750	Moisture of wood 12.1 %
A7a,b	30	Light	3000	Moisture of wood 11.8 %
A8a,b	29	Light	1500	Moisture of wood 12.4 %
A9a,b	28	Light	750	Moisture of wood 12.2 %
A10a,b	10	Intensive	1500	Moisture of wood 10.5 %
A11a,b	11	Intensive	1500	Moisture of wood 15.7 %
A12a,b	12	Intensive	1500	Moisture of wood 18.3 %
A13a,b	13	Intensive	1500	Moisture of wood 25.3 %

A14a,b	14	Intensive	1500	Moisture of wood 28.2 %
A15a,b	21	medium	1500	Moisture of wood 9.8 %
A16a,b	21	medium	1500	Moisture of wood 19.0 %
A17a,b	21	medium	1500	Moisture of wood 20.3 %
A18a,b	21	medium	1500	Moisture of wood 25.9 %
A19a,b	21	medium	1500	Moisture of wood 29.4 %
A20a,b	28	light	1500	Moisture of wood 10.0 %
A21a,b	29	light	1500	Moisture of wood 19.0 %
A22a,b	28	light	1500	Moisture of wood 19.5 %
A23a,b	28	light	1500	Moisture of wood 25.2 %
A24a,b	28	light	1500	Moisture of wood 24.0 %
(B) casing types (12 samples, 8 smoking experiments)				
B1a,b,c,d	12	intensive	3000	Sheep casing and cellulose casing
B2a,b,c,d				
B3a,b,c,d	12	intensive	3000	Collagen casing
(C) fat contents (48 samples, 12 smoking experiments)				
C1a,b	12	intensive	3000	Fat content (10-39 %)
C2a,b	12	medium	1500	Fat content (10-39 %)
C3a,b	15	Intensive	3000	Fat content (10-39 %)
C4	14	Intensive	3000	Fat content (10-39 %)
C5	13	Intensive	3000	Fat content (10-39 %)
C6	12	Intensive	750	Fat content (10-39 %)
C7	13	Intensive	750	Fat content (10-39 %)
C8	13	Intensive	1500	Fat content (10-39 %)
C9	14	Intensive	1500	Fat content (10-39 %)
(D) wood types (29 samples, 29 smoking experiments)				
D1-D10	12	Intensive	3000	oak, poplar, hickory, spruce, fir, alder, beech beech with apple-smoking spice mix beech with cherry-smoking spice mix beech with a mix of juniper berries and bay leaves

The Frankfurter-type sausages were reddened for 10 min at 52 °C, dried for 12 min at 56 °C, and then smoked for 12 min at 58 °C. For the experiments investigating the different smoking conditions (A) the chosen smoking time was dependent on the smoking intensity. Three different smoke densities were tested: intensive smoke, medium smoke and light smoke. Also three different ventilator velocities (750, 1500 and 3000 rpm) were applied. The smoking time of the different experiments was adjusted to the different smoking conditions (A) to obtain Frankfurter-type sausages of comparable colour. After smoking the sausages were scalded for 25 min at 75 °C. For chemical analysis 2.25 kg of the smoked sausages were homogenised in a bowl chopper and placed in sterile side seal vacuum bags from Gruber-Folien (Straubing, Germany) and stored in the dark at -18 °C.

Measurement of the smoke generation temperature and the gases

The data acquisition of the gas detection in the smoking chamber and the temperature of wood combustion were performed with a 350-S flue gas analyser and a NiCrNi sensor from Testo (Lenzkirch, Germany). The concentrations of oxygen and CO_2 were measured in volume percent, and concentrations of CO were quantified in ppm. The gas concentrations were recorded during the entire smoking process, averaging one value every 5 s.

Measurement of the pH value and the colour

The pH-value of the smoked sausages was measured using a Portamess Type 911 pH meter from Knick (Berlin, Germany). A Minolta CR-400 colorimeter (Osaka, Japan) was used to determine the meat colour [L* (lightness), a* (redness) and b* (yellowness)] of the produced sausages. In addition, pictures of the produced sausages were taken.

Analysis of the contents of PAH and phenolic compounds

The PAH contents were determined using a previously published method [4]. The contents of the phenolic compounds guaiacol, 4-methylguaiacol, syringol, eugenol, and *trans*-isoeugenol were determined using an analytical method including steam distillation, clean-up on a silica cartridge, trimethylsilylation and analysis by GC/MS [4].

III. RESULTS AND DISCUSSION

Analysis of pH, colour and weight loss

The results of pH-values, weight losses and L*a*b*-values for the Frankfurter-type sausages are shown in Table 3.

Table 3 Results of pH, weight losses, and colour analysis of the different smoking experiments

	pH	Weight loss [%]	L*-value	a*-value	b*-value
(A) smoking conditions					
Light smoke	6.4	9.7	61.5	19.3	23.7
Medium smoke	6.4	9.5	59.2	20.5	25.5
Intensive smoke	6.4	8.2	59.2	20.2	28.7
(B) casing types					
Cellulose casing	6.05	6.6	56.6	18.7	29.2
Sheep casing	6.12	7.8	57.0	18.2	31.5
Collagen casing	6.04	6.0	54.3	20.1	33.9
(C) fat contents					
9.9%	6.06	9.3	49.0	22.1	30.9
19.6%	6.07	8.7	52.3	21.0	32.4
29.5%	6.06	7.2	56.3	19.1	33.5
39.1%	6.07	6.5	57.8	18.0	33.2
(D) wood types					
Beech	6.17	7.7	56.2	18.1	29.7
Oak	6.11	8.0	56.0	18.8	30.2
Spruce	6.05	7.7	57.0	18.9	33.5
Poplar	6.12	7.0	54.7	20.2	33.9
Alder	6.26	8.1	59.9	17.1	32.6
Hickory	6.09	7.6	53.4	20.1	29.6
Fir	6.05	8.0	60.5	16.5	30.8
Apple spice mix	6.23	7.2	58.1	18.5	36.0
Cherry spice mix	6.07	7.2	56.6	19.2	33.9
Juniper berries & bay leaves	6.22	7.7	57.2	18.7	33.5

The pH-values of the Frankfurter-type sausages of the experiments investigating different smoking conditions (A) were 6.4, for the smoking experiments with different casing types (B), fat contents (C), and wood types (D) in the range from 6.04 to 6.26. For lightly smoked sausages the weight loss was a little higher (9.7%) as a result of longer smoking times. The higher the fat content was in the Frankfurter-type sausages, the lower the weight loss was. Comparing different types of wood, the lowest weight loss was observed for sausages smoked with poplar wood chips.

Correlation between smoking conditions and PAH contents

In the present study, the focus was primarily on BaP and PAH4 (sum content of BaP, BaA, CHR, and BbF). For experiments 1 to 9 the original wood chips (manufacturer information: 12.5% moisture) with a determined moisture between 11.8 and 13.0% were used. The contents of PAH4 were depending on the ventilator velocity and the smoke density (Pöhlmann et al., 2012). An increase in the ventilator velocity (750 rpm to 3000 rpm) and smoke density resulted in higher PAH4 contents.

An increase in the smoke density was more relevant than an increase in the ventilator velocity. The PAH4 mean contents of intensively smoked samples with a ventilator velocity of 1500 and 3000 rpm were very similar (2.96 and 2.90 µg/kg, respectively). A differentiation between sausages produced in the first (a) and second (b) smoking experiments using the same smoking conditions showed that the PAH4 contents in samples of the first accomplished smoking experiment increased linearly with faster ventilator velocity. The PAH4 contents in sausages of the second experiment showed an outlier for a ventilator velocity of 1500 rpm, which was significantly higher than expected (3.3 µg/kg). The lowest PAH4 content (1.1 µg/kg) was detected in sausages applying light smoke and a ventilator velocity of 750 rpm.

In experiments 1-9 the contents of BaP (0.11-0.48 µg/kg) and PAH4 (1.10-2.96 µg/kg) showed comparable tendencies. As mentioned before, the ventilator velocity and the smoke density influenced directly the smoke generation temperature and the concentrations of CO, CO_2 and O_2 in the smoking chamber. A higher maximum of smoke generation temperature resulted in higher BaP and PAH4 contents (Fig. 1).

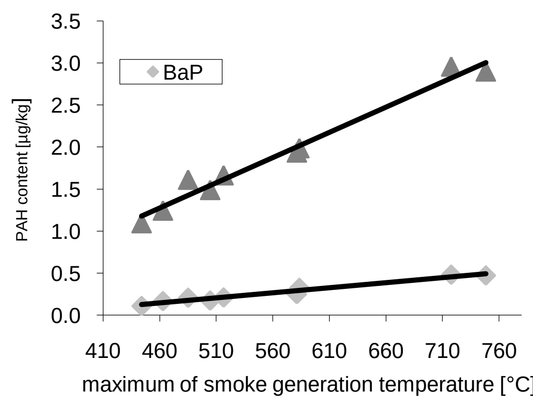

Figure 1 Correlations between maximum of smoke generation temperature [°C] and contents of BaP and PAH4 [µg/kg]

The maximum of smoke generation temperature showed a correlation to the PAH4 contents (R^2 = 0.98) and BaP contents (R^2 = 0.96). A higher smoke generation temperature also correlated with higher carbon monoxide and carbon dioxide levels but lower oxygen levels. Consequently the BaP and PAH4 contents were also proportional to the CO and CO_2 levels and inversely proportional to the oxygen level.

For the smoking experiments at different moisture contents of the beech wood chips the ventilator velocity was set at 1500 rpm and the moisture to 10, 15, 20, 25, and 30%. Increasing the moisture levels in the beech wood chips resulted in lower smoke generation temperatures. Although smoking experiments at a constant moisture content of the wood chips showed a correlation between smoke generation temperature and PAH contents, a correlation between the moisture of the wood chips and PAH content could not be observed.

Correlation between type of casing and PAH contents

Within the experiments [4] different types of casings (peelable cellulose, sheep, and collagen) were used. Frankfurter-type sausages with peelable cellulose casings showed the following PAH contents: 0.75 ± 0.19 µg/kg (PAH4) and 0.09 ± 0.03 µg/kg (BaP). The sausages with the sheep casings had higher PAH contents than the peeled cellulose sausages and contained 3.59 ± 1.09 µg/kg (PAH4) and 0.57 ± 0.21 µg/kg (BaP). The sausages in collagen casings showed a similar contamination level as the products in cellulose casings: PAH4: 2.98 ± 0.63 µg/kg and BaP: 0.40 ± 0.12 µg/kg (Fig. 2)

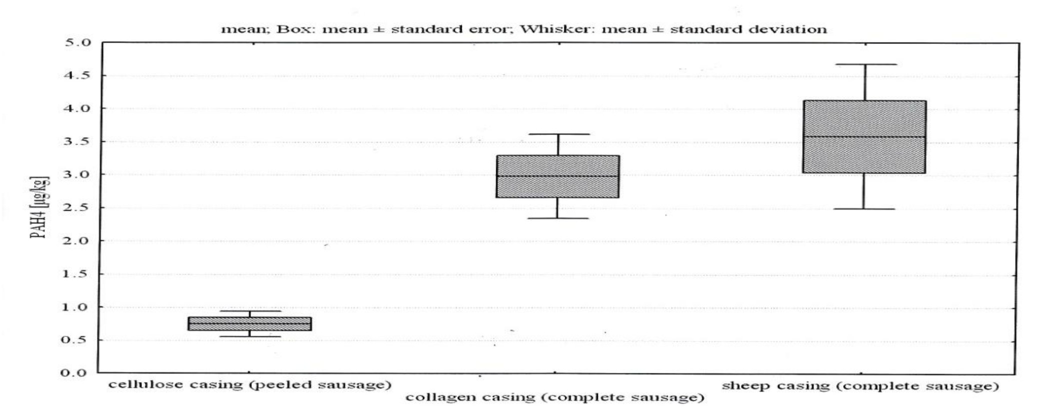

Figure 2 PAH4 contents [µg/kg] in Frankfurter-type sausages in cellulose casing (peeled sausage), collagen sausage (complete sausage), and sheep casing (complete sausage) (N=4)

The cellulose casings (without sausage) were also analysed and contained high PAH contents compared to the PAH contents in the stuffing of the sausages (PAH4: 81 ± 31 µg/kg and BaP: 23 ± 11 µg/kg). A cellulose casing accounted for about 1.5% of the weight of a total Frankfurter-type sausage before peeling. Considering the different weight proportions of the cellulose casing and the edible part of the sausage in relation to the PAH content, the complete Frankfurter-type sausages (with cellulose casings) would have contained 1.95 ± 0.58 µg/kg PAH4 and 0.43 ± 0.19 µg/kg BaP. Consequently, the cellulose casings contained 61 ± 11 % of the total PAH4 content and 77 ± 7 % of the total BaP content of an unpeeled Frankfurter-type sausage. The tendency of being accumulated in the cellulose casings was stronger for the five-ring molecules BbF and BaP than for the four-ring molecules BaA and CHR.

Correlation between fat content and PAH contents

The different fat contents in Frankfurter-type sausages led to different PAH contents [4]. Increasing the back fat content from 9.9% to 19.6%, to 29.5%, and up to 39.1% the mean PAH4 content also increased from 2.4 ± 0.7 µg/kg to 3.2 ± 1.2 µg/kg, to 3.7 ± 0.9 µg/kg, and up to 3.9 ± 0.9 µg/kg. The same tendencies were observed for BaA, CHR, BbF, and BaP.

For a better comparability of different smoking conditions, the PAH4 content in Frankfurter-type sausages with a back fat content of 39.1% was set to 100%, and the other three remaining

PAH4 contents of the same smoking experiment were compared to this value in percent.

To check the influence of the back fat contents of the sausages on the PAH contents in dependency on the absolute PAH4 content, three groups were formed: the first group consisted of the four lowest PAH4 contents for sausages with 9.9% back fat (PAH4 < 2 µg/kg), the second group of the four medium PAH4 contents for sausages with 9.9% back fat (2 µg/kg < PAH4 < 2.5 µg/kg), and the third group of the four highest PAH4 contents for sausages with 9.9% back fat (PAH4 > 2.5 µg/kg). The relative PAH4 contents of the first group with low PAH4 contents and the second group with medium PAH4 contents increased with increasing back fat contents, showing a similar behaviour: The PAH4 contents increased from 55% (back fat content: 9.9%) to 72% (back fat content: 19.6%) and up to 91% (low) and 93% (medium), respectively (back fat content: 29.5%) (Fig. 3).

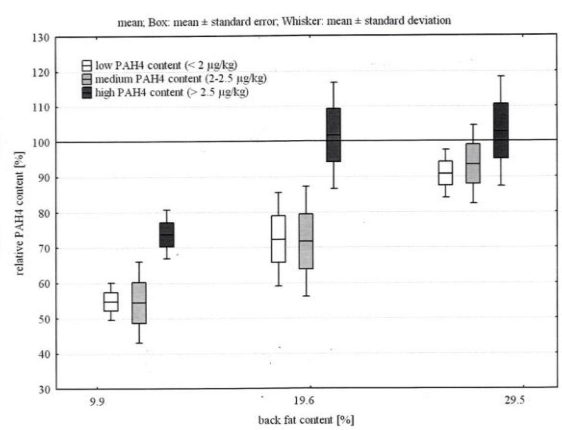

Figure 3 Correlation between normalised PAH4 contents (39.1 % fat = 100 %) and fat content in Frankfurter-type sausages with low (<2 µg/kg), medium (2-2.5 µg/kg), and high (> 2.5 µg/kg) PAH4 contents (N = 4, each)

In contrast, sausages of the third group with high absolute PAH4 contents showed similar relative PAH4 contents for back fat percentages of 19.6% and 29.5% (102% and 103%, respectively). With respect to back fat contents of 39.1%, only sausages with 9.9% back fat had a lower relative PAH4 content (74%).

Correlation between type of wood and PAH contents

According to a report of the EFSA (EFSA, 2008), beech wood is the most common wood applied for smoking of foodstuffs. Consequently, the PAH contents of the Frankfurter-type sausages smoked with beech wood were compared to those smoked with other types of wood (Hitzel et al., 2013). Beech wood resulted in the following PAH contents: 0.71 ± 0.08 µg/kg BaP and 4.30 ± 0.45 µg/kg PAH4. The mean contents of BaP and PAH4 in Frankfurter-type sausages smoked with alder (BaP: 0.80 ± 0.15 µg/kg, PAH4: 4.70 ± 0.49 µg/kg), and with beech + cherry spice mix (BaP: 0.73 ± 0.25 µg/kg, PAH4: 4.33 ± 0.92 µg/kg) were slightly increased compared to sausages smoked with beech wood (see Fig. 4). The use of the other tested types of wood resulted in lower PAH contents than in beech wood smoked sausages. A reduction of the contents of BaP and PAH4 greater than 30%, compared to the use of beech wood chips, was observed for poplar, hickory, and beech wood spiced with an apple spice mix. For the other types of wood only lower reductions in the PAH contents were observed.

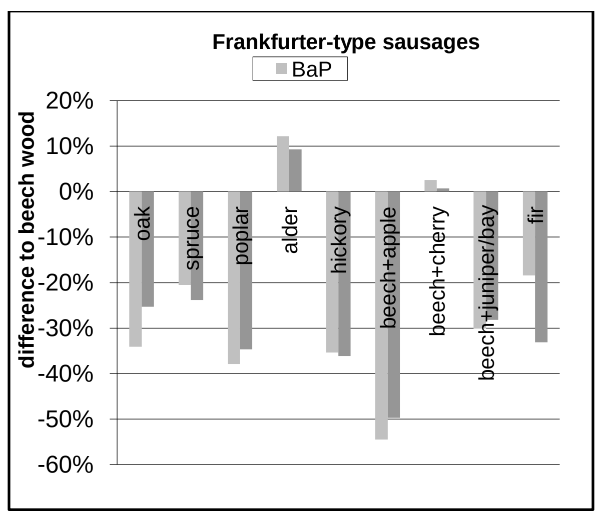

Figure 4 Mean percental deviations of BaP and PAH4 contents in Frankfurter-type sausages smoked with different types of wood compared to beech wood

IV. CONCLUSION

Minimization of PAH compounds in hot smoked sausages using glow smoke is possible. Lowering the contents of PAH compounds does not necessarily lead to a decrease in the amounts of phenolic substances as correlations between the contents of PAH and phenolic compounds were not observed. The most important parameter influencing PAH contents is the smoke generation temperature. Therefore, accurate control of the smoke generation temperature to achieve low smoke generation temperatures (below 600 °C) is a promising approach to lower PAH contents in hot smoked sausages. As a consequence of the reduction of the smoke generation temperature longer smoking times with higher weight losses are required to obtain a comparable colour. Due to the poor smoky odour and especially smoky flavour the smoke generation temperature should not be lowered to below 500 °C. An increase in wood chip moisture content seems not to be a reasonable approach for reducing PAH contents in hot smoked sausages using glow smoke, since no correlation between the moisture of the wood chips and the PAH contents of the smoked sausages was observed.

The selection of a cellulose-peelable casing is a reasonable approach for reducing the PAH contents in hot smoked sausages as a high percentage of the PAHs (BaP: 77%; PAH4: 61%) remains in the peelable casing and does not penetrate into the interior of the meat product. In contrast, the major part of the phenolic compounds (about 99%) penetrates into the inside of the sausage. A comparison of the sausages in sheep casing and collagen casing showed that the sum content of phenolic compounds was twice as high for sheep casings and the PAH contents were nearly at the same level. A reduction of the PAH compounds in hot smoked Frankfurter-type sausages by lowering the back fat contents in the formulation of the sausages is also possible. In spite of the higher weight losses of sausages with lower fat contents, the PAH contents in these sausages were lower. A decrease in the amounts of phenolic substances was not observed by lowering the back fat contents in Frankfurter-type sausages as very similar contents of phenolic compounds were detected in sausages of all fat contents.

The selection of an alternative wood species to the most commonly used beech wood seems to be a reasonable approach for reducing the PAH contents in hot and cold smoked sausages, since smoking with all types of wood (with the exception of alder and beech wood spiced with cherry smoking spice) resulted in lower PAH contents compared to beech wood smoked sausages. The lowest PAH contents were detected in sausages smoked with poplar and hickory wood chips. The use of poplar and hickory wood chips led to a decrease in the contents of BaP and PAH4 in the range of 35–40% compared to the use of beech wood chips. However, the sum contents of the five phenolic compounds in sausages smoked with poplar and hickory wood chips were higher or only slightly lower than in sausages smoked with beech wood chips. Especially the use of poplar wood chips seems to be an interesting alternative, since, on the one hand poplar is a rapidly growing type of wood, on the other hand the low volumetric heating value of this wood species might be an advantageous property for obtaining relatively low smoke generation temperatures and consequently low PAH contents.

ACKNOWLEDGEMENTS

This research project was supported by the German Ministry of Economics and Technology (via AiF) and the FEI (Forschungskreis der Ernährungsindustrie e.V., Bonn). Project AiF 16460N and the Förderergesellschaft für Fleischforschung e.V. The authors would like to thank Gertrud Eigner, Elisabeth Klötzer, Lisa Schwitz, and Sandra Ziegler for their excellent technical assistance, Bertram Schregle for producing the sausages and performing the smoking experiments, and Fessmann GmbH und Co KG (Winnenden, Germany) for providing the smoking chamber.

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