



Effect of two fish smoking ovens on the nutritional composition and PAH content of smoked fish

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ABSTRACT

The quality of three marine fish species smoked with a gas smoker (Abuesi Gas Fish Smoker) and a fuelwood smoker (Chorkor Smoker) were analyzed. The aim was to evaluate the nutritional profile and Polycyclic Aromatic Hydrocarbon (PAH) levels in smoked fish from these smokers. The three fish species were the yellowfin tuna *Thunnus albacares*, the common white grouper *Epinephelus aeneus* and barracuda *Sphyraena sphyraena*. The Abuesi Gas Fish Smoker produced significantly better quality-smoked fish than the Chorkor smoker. The protein, moisture, fat, total carbohydrate and ash contents of the gas smoked fish were in the range of 54.23 - 70.32%, 13.69 - 24.73%, 5.28 - 8.76%, 2.97 - 13.21% and 2.77 - 4.27% respectively, whilst that of the fuelwood-smoked fish were 43.38 - 43.75%, 22.00 - 46.5%, 2.00%, 5.26 - 25.78% and 2.85 - 6.50% respectively. Total PAH concentration ranged between 321.7 - 514.41 µg/kg for gas-smoked fish and 1038.8 - 1550 µg/kg for fuelwood-smoked fish. PAH concentrations per fish species in the two different fish smokers were significantly different. The EU maximum residue limits (MRLs) for PAH4 and BAP were met in the Gas Fish Smoker but not in the Chorkor Smoker. It is concluded that the gas fish smoker is a better choice, in terms of fish quality, than the fuelwood smoker.

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Introduction

Fish is highly perishable and must be handled properly and well preserved after harvest, in order to remain fit for human consumption ^[1]. Globally, various methods are used for fish preservation such as freezing, cooling, drying, salting, smoking and canning. In West Africa and particularly Ghana, smoking at temperatures above 80°C is the most common method of fish preservation. Smoked fish represent an estimated 70 - 80% of all marine and freshwater fishes consumed in the country ^[2].

The Chorkor smoker is the most popular traditional oven used in Ghana for fish smoking. Fish smoking using this oven involves the treatment of pre-salted fish with smoke from incomplete combustion of wood at high temperatures ^[2]. However, Idah and Nwankwo ^[3] noted that very high smoking temperatures can affect the nutritional content of smoked fish and emphasized the need for assessment of the nutritional properties of fish smoked from ovens that produce high temperatures such as the Chorkor smoker. In addition, high levels of Polycyclic Aromatic Hydrocarbons (PAHs) released through direct contact of fish with combustion gases can occur when using this smoker ^[4].

PAHs are complex chemical compounds formed and released during incomplete combustion or pyrolysis of organic matter ^[5]. They have received much attention over the years and known for their harmful effects on human health with some known to be carcinogenic ^[4]. The International Agency for Research into Cancer reported benzo[a]pyrene as a human carcinogen ^[5].

Essumang *et al.* ^[6] conjectured that the high intake of smoked fish in the Ghanaian diet could contribute to the increase in cancer cases in the country, especially, breast cancer in the older female population.

In order to reduce the adverse effects of PAHs in smoked fish on the health of consumers, maximum residue limits (MRLs) of PAHs are set for smoked fish and smoked fish products. The maximum limits set for benzo[a]pyrene and PAH4 are 2.0 µg/kg and 12.0 µg/kg respectively ^[7].

The aim of this study is to compare the effect of the Chorkor smoker (a fuelwood oven) with that of the Abuesi gas fish smoker (a liquefied petroleum gas oven) on the quality of smoked fish produced.

Materials and Methods

Sample Collection

Raw fish samples of three different species common in Ghana, namely barracuda (*Sphyraena sphyraena*, Sphyraenidae) (Linnaeus, 1758), common white grouper (*Epinephelus aeneus*, Serranidae) (Geeoff. St. Hill, 1809), and yellowfin tuna (*Thunnus albacares*, Scombridae) (Bonnat, 1788) were purchased from fishmongers at Abuesi in the Western Region and Tema fishing harbour at Tema in the Greater Accra Region of Ghana in September 2016. These fish species are consumed largely in the smoked form.

Description of the Fish Smokers

The Chorkor smoker is a traditional fish smoking oven well known and commonly used in Ghana. It consists of a combustion chamber and a smoking unit with a set of trays. The combustion chamber is rectangular, twice as long as it is wide and divided by a wall down the middle and with two stoke holes in front. The recommended standard measurements of the combustion chamber are: 225 cm (length), 112.5 cm (width), 60 cm (height), 12.5 cm (wall thickness), 37.5 cm (width and height of stoke hole) and 15 cm (depth of fire pit). The combustion chamber is at the base of the smoker and constructed from mud, although burnt bricks and cement blocks may be used. The top of the wall

must be flat so that the wooden trays can sit firmly on it without burning.

The smoking unit consists of a set of 5-15 smoking trays, depending on the size and type of fish to be smoked [12].

The Abuesi Gas Fish Smoker on the other hand is a liquefied petroleum gas (LPG) operated fish smoker. It is a double chamber oven with the dimensions of 1.2 m x 2.4 m x 1.8 m (Length x Height x Width). The frame is made of a stainless steel to prevent rusting. At the bottom of each chamber is a perforated metal coil through which the gas burns to heat the entire oven. The oven is also equipped with a thermometer for temperature determination. Within each chamber is a suction fan that sucks moisture from the oven since the heated oven moderately cooks the fish during the process of smoking. Within each chamber are a number of grooves to support trays for smoking the fish. The oven also has a bowl at the base of the coil, which can be filled with wood chippings to generate smoke during smoking. A fully loaded oven takes about 0.7 tons of fish and the smoking process can be accomplished in two hours [18].

Fish Smoking Processes

Fresh fish samples of the different species: barracuda, common white grouper and yellowfin tuna were weighed, descaled, gutted, washed thoroughly with clean water and cut in smaller pieces for smoke curing. The cut fish samples were dipped in salt solution and drained. The different fish samples were then arranged on separate trays and smoked in the Abuesi Gas Fish Smoker and the Chorkor smoker in triplicates. The smoked fish samples were packaged and kept at room temperature for the laboratory analysis.

Proximate Composition

For each of the samples smoked by the two fish smokers, the moisture content, crude protein, crude lipid, total carbohydrates and ash content were determined using the method of analysis as described by the Association of Official Analytical Chemists [19]. Samples were taken from the dorsal, anterior section and mid region of the fish. The data were analysed statistically by t Test: Paired two samples for means to determine mean differences between crude protein, fat content, moisture content, total carbohydrates and ash content of the fish samples from the two smoking methods.

PAH Analysis

For each of the fish samples smoked using the two ovens, 16 PAHs were targeted: (Naphthalene (NAP), Acenaphthalene (ACA), Acenaphthene (ACE), Fluorene (FLU), Phenanthrene (PHE), Anthracene (ANT), Fluoranthene (FLT), Pyrene (PYR), Chrysene (CHR), Benzo(b)fluoranthene (BBF), Benzo(k)fluoranthene (BKF), Benzo(a)pyrene (BAP), Indeno(1,2,3,c,d)pyrene (IND), Dibenzo(a,h)anthracene (DAA), Benzo(g,h,i)perylene (BGP) and Benzo(a)anthracene (BAA). These 16 parameters were targeted because they are the commonly occurring PAHs. The Agilent Bond Elut QuEChERS extraction procedure was used. This method was chosen because it is easy, less expensive and is validated in terms of accuracy, specificity, linearity and quantification

limits [10]. Fish samples per species weighed between 120 g to 200 g. The samples were deboned, blended, bagged and labeled. 5 g of each of the samples was weighed with a Mettler Toledo PG1003-S electronic balance into a Poxgrid 15 ml conical tube. 10 ml of Acetonitrile was added to each of the samples for extraction and homogenized for one minute using Ultra turrax homogenizer IKA- T25. 6 g of Magnesium sulphate and 1.5 g sodium chloride salts were added to the samples and shaken for one minute using the Vortex mixer for liquid-liquid partitioning.

The samples were centrifuged for five minutes using a Hermle Z300 centrifuge at a speed of 4RPM. 6 ml of the organic layer was put into a Poxgrid 15 ml conical tube after separation and c18 (high performance liquid chromatography or HPLC), magnesium sulphate and primary secondary amines (PSA) added for cleanup and shaken for 30 seconds. The sample was centrifuged again for 5 minutes at a speed of 4RPM. 4 ml of the sample was put into a pear-shaped flask. The sample was then put in Buchi rotary evaporator for evaporation below 40°C. The sample was redissolved in 1 ml acetonitrile and put in an ultra-sonic water bath to knock the sample stuck to the walls of the flask into the reagent. The sample was put into a 2 ml GC val for analysis of PAHs. A Gas Chromatograph - Mass Spectrometry (GC/MS) was used for the analysis. The total PAHs, BaP, PAH4, as well as, the sum of 8 SCF -15, which have been deemed genotoxic compounds by the European Scientific Committee on Foods were calculated [5].

Results and Discussion

Proximate composition

The result of the proximate analysis carried out on the smoked fish is presented in Table 1. The average values of the crude protein, fat content and ash were generally higher in the gas smoked samples. The results however showed a decrease in moisture content of the gas smoked fish compared to those smoked with wood. Moisture content is one of the factors that can be used as an indicator of the rate at which deterioration occurs in fish samples resulting in early decomposition [11]. The moisture content of the gas smoked fish samples were less than 25% while the moisture content of the wood smoked fish samples were above 25% except for the white grouper. It has been documented that well dried fish with moisture reduced to 25% (wet weight) can be preserved for a longer period of time as microbial activities are retarded [12]. It can be seen from the results that safe moisture content was achieved in all gas smoked fish products.

The crude protein was significantly higher in the gas smoked fish samples than in the wood smoked fish samples. The increase in crude protein could be attributed to its concentration in the fish, as a result of the relatively higher loss of moisture in the gas smoked samples from the smoking process. This inference falls in line with Aliya *et al.* [13] who stated that there is an inverse relationship between protein and moisture content i.e. protein content increases as moisture content decreases.

Table 1. Percent proximate composition of fish smoked with the Abuesi gas fish smoker (A) and the Chorkor smoker (C). Values are mean percentages \pm SD. Significance between treatments are indicated by different letters across columns A and C.

Species	Crude Protein		Crude fat		Total carbohydrates		Moisture content		Ash content	
	A	C	A	C	A	C	A	C	A	C
<i>Thunnus albacares</i>	54.23 \pm 0.71 ^a	43.75 \pm 0.01 ^b	5.28 \pm 0.74 ^a	2.00 \pm 0.00 ^a	13.21 \pm 0.28 ^a	5.26 \pm 2.82 ^a	24.73 \pm 0.09 ^a	46.5 \pm 2.12 ^b	2.7 \pm 0.04 ^a	2.50 \pm 0.71 ^a
<i>Epinephelus aeneus</i>	61.14 \pm 0.53 ^a	43.73 \pm 0.04 ^b	7.05 \pm 0.21 ^a	2.00 \pm 0.00 ^b	6.49 \pm 0.59 ^a	25.78 \pm 2.09 ^a	22.48 \pm 0.21 ^a	22.00 \pm 2.83 ^a	2.85 \pm 0.06 ^a	6.50 \pm 0.71 ^a
<i>Sphyraena sphyraena</i>	70.32 \pm 0.12 ^a	43.38 \pm 0.53 ^b	8.76 \pm 0.15 ^a	2.00 \pm 1.41 ^b	2.97 \pm 0.49 ^a	13.13 \pm 3.01 ^b	13.69 \pm 0.43 ^a	38.50 \pm 2.12 ^b	4.27 \pm 0.04 ^a	3.00 \pm 0.00 ^a

Holma and Maalekuu ^[14] stated that a high crude protein content in fish offered high dietary status due to the essential amino acids they provide.

Idah and Nwankwo ^[3] reported lower fat content of wood smoked fish and attributed it to high smoking temperatures in the oven. This could be the probable reason for the lower fat content in fish processed with the Chorkor smoker as compared to the gas smoker in this study.

There was no significant difference between the total carbohydrates content of the gas and wood smoked fish samples. The amount of carbohydrate in fish is generally too small to be given any significance in a diet ^[15].

Ash content is a measure of the total amount of minerals present in the fish. There was no significant difference between the ash content of the gas smoked fish and wood smoked fish samples except in the barracuda where the ash content was significantly higher in the gas smoked fish than the wood smoked fish. This could mean that the gas and wood smokers had relatively similar effects on the fish samples.

PAHs Assessment

Table 2 reports concentrations ($\mu\text{g/kg}$) of each single PAH in both gas and wood smoked samples. All 16-targeted PAHs were detected in the wood smoked fish except acenaphthalene. The total PAHs, BaP, PAH4 and 8 SCF -15 were higher in the wood smoked samples. The PAH with the highest concentration in the gas smoked samples was naphthalene. The PAHs not detected (nd) were assumed to be absent in the fish samples.

Higher concentration of PAHs was seen in the wood smoked fish samples. This is in line with report by Akpambang *et al.*, ^[4](2009) that direct smoking of fish, using fuelwood at high heating temperatures may be responsible for high PAH levels in processed foods. More PAHs were also detected in the wood smoked samples than the gas smoked samples, this demonstrates that burning log fire may introduce many PAHs to the finished product when used for fish smoking. The level of contamination was largely reduced when fish was smoked using gas as the source of fuel. It seems more likely that the use of gas instead of burning wood, as a source of fuel could reduce the level of PAHs contamination in smoked fish products. The different levels

of PAHs in fish smoked by the two methods is in line with report by Visciano *et al.* ^[16] that the type of combustible used affects the PAH levels in smoked fish products.

Even though the total concentration of PAHs was higher in the wood smoked fish samples than the gas smoked ones, the total PAHs concentration of the gas smoked fish samples was quite high, and exceeding 300 $\mu\text{g/kg}$ in all the gas smoked fish samples. This relatively high PAHs concentration in the gas smoked fish samples was mainly as a result of high naphthalene concentrations.

The ratio of fluoranthene to pyrene was greater than one (FLT/PYR>1) in all the fish samples. This dictates that the PAHs detected could be attributed to pyrolytic sources as reported by Amos-Tautua *et al.*, ^[17]. Also, all samples analyzed had similar PAH profile for each smoking method, and could indicate that sources of contamination of the samples were the same for each smoking method.

All the 8 targeted SCF-15 PAHs considered to be potentially genotoxic and carcinogenic to humans ^[5], were found in the wood smoked fish samples while only two were found in the gas smoked fish, except for the gas smoked tuna which had six. The individual PAHs concentrations were also higher in the wood smoked fish samples. This result indicates that using wood as the source of fuel introduced higher concentrations of potentially genotoxic and carcinogenic PAHs to the finished product.

Compliance with EU MRL

From the results, gas smoked fish samples were within the specified limits for PAH4 and BAP, whereas the wood smoked samples had PAH4 and BAP concentrations far exceeding the EU MRL limits. Other researchers have reported high BAP levels in wood smoked fish. Essumang *et al.* ^[6] and Akpambang *et al.* ^[4] reported BAP levels ranging from 8.5 $\mu\text{g/kg}$ and 73.78 $\mu\text{g/kg}$ and 2.4 $\mu\text{g/kg}$ and 31.3 $\mu\text{g/kg}$ respectively in traditionally smoked fish samples. The presence of high levels of BAP in the wood smoked fish samples is an indication of heavy contamination of commonly consumed smoked fish in Ghanaian diets. This may imply an increased risk of carcinogenic and mutagenic hazards in the Ghanaian population ^[6].

The non-compliance of the traditionally smoked fish in this study to EU standards also means that such

Table 2. Summary of concentrations of PAHs ($\mu\text{g/kg}$) in fish smoked with the Abuesi gas fish smoker (A) and the Chorkor smoker (C). The European Union maximum residual limit (EU MRL) is only for most important components, PAH4 and BAP.

.PAH compound (abbreviated)	<i>Thunnus albacares</i>		<i>Sphyraena sphyraena</i>		<i>Epinephelus aeneus</i>		EU MRL ($\mu\text{g/kg}$)
	A	C	A	C	A	C	
NAP	482.6	2.2	440.1	69.2	251	52.3	
ACA	1.56	43.7	2.1	88.5	1.7	45.5	
ACE	nd	nd	nd	nd	nd	nd	
FLU	0.28	34.6	0.92	93.8	nd	67.8	
PHE	nd	252.5	nd	79.2	22.4	59.6	
ANT	nd	251.5	0.4	383.1	27.1	273.8	
FLT	16.8	125.6	17.5	208.2	11.6	152.9	
PYR	0.27	125.1	9.2	208	7.7	152.1	
CHR	3.1	69.7	2.3	420.4	0.2	142.3	
BBF	0.5	26.1	nd	66.5	nd	49.4	
BKF	1.3	25.3	nd	70.3	nd	49.9	
BAP	1.4	26.7	nd	71.1	nd	50.3	
IND	nd	9.1	nd	18.6	nd	14.2	
DAA	nd	9.4	nd	18.1	nd	14.1	
BGP	3.4	9.3	nd	18.5	nd	14.2	
BAA	3.2	73	2.4	307.7	0.1	123.8	
TOTAL PAH	514.41	1038.8	474.9	1550.4	321.7	1262.2	
Total BAP	1.4	26.7	nd	71.1	nd	50.3	2
Total PAH4	8.2	195.5	4.7	865.7	0.3	365.8	12
FLT/PYR	62.2	1.0	1.8	1.0	1.5	1.0	
Sum of 8 SCF-15	12.9	248.6	4.7	991.2	0.3	408.3	

nd: not detected; LOD: 0.01 $\mu\text{g/kg}$

processed fish products cannot be exported to the EU market.

Conclusion

The nutritional quality of fish processed with the Abuesi gas fish smoker was better than those smoked with the wood smoker. The most significant observations were the high crude protein in the gas smoked fish and the low PAH levels that met the EU limits. This means that fish smoked with the gas fish smoker is comparatively healthier for consumption in the Ghanaian diet.

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