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Comparison of PAHs Formed in Firewood and Charcoal Smoked Stock and Cat Fish

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Abstract Polycyclic aromatic hydrocarbons (PAHs) are a product of incomplete combustions. Foods prepared via combustion and high temperature are linked with incomplete combustion making them vulnerable to having PAHs in their constituent. Two species of fish: stock fish and cat fish were bought from Ogbomoso and smoked using firewood and charcoal at various time intervals. The processed samples were extracted using ultrasonicator and the extracts separated using n-hexane, mixture of dichloromethane and n-hexane (3:2). The identification and concentration of PAHs were carried out using Gas chromatography coupled with flame ionization detector (GC/FID) while the proximate analysis was done according to the standard described by AOAC, 2002. The GC/FID analysis showed that 24 PAHs were found in all the samples except Naphthalene and benzo (j) fluoranthene which were not detected in firewood smoked stock fish and charcoal smoked cat fish respectively at various smoking time. The total concentration of PAHs in firewood smoked stock fish (FSSF) ranged from 7.36 – 16.84 mg/kg, total concentration in charcoal smoked stock fish (CSSF) ranged from 1352.23 – 1736.06 mg/kg while the total concentration in firewood smoked cat fish (FSCF) ranged from 91.22 – 1248.77 mg/kg and PAHs concentrations in charcoal smoked cat fish (CSCF) ranged from 200.11 – 1847.44 mg/kg. The proximate analysis revealed that, the highest moisture content (63.25 %) in all the samples was obtained in FSCF 1h, highest protein content (65.94 %) obtained in CSSF 4h, highest fat (28.15 %) obtained in FSCF 4h. The molecular indices ratio suggested that the PAHs were from pyrolytic source.

Keywords: *smoked, extracted, time intervals, PAHs concentration, proximate analysis*

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1. Introduction

Perishable foodstuffs have been smoked in many countries for centuries. Originally, smoking was done to preserve the food; by reducing the moisture content and partly through the transfer of anti-microbiological components, such as aldehydes and phenols, from the smoke to the food [1]. Now, the present purpose of smoking includes impacting characteristic taste and appearance of smoked food, with preservation playing a minor role [1,2]. Smoking of fish is a common processing technique in use owing to its low investment cost and ease of manipulation. Smoking is an ancient preservation method for fish and other meats. Fish is typically salted before being dried and smoked. Both salting and drying lower the water activity in the fish. In addition, smoking introduces antioxidant and bacteriostatic effects to the fish thus extending its shelf-life.

Smoking food items in uncontrolled processing conditions, characteristic for traditional smoking process, results in high concentrations of polycyclic aromatic hydrocarbons (PAHs) [1,2,3,4]. PAHs are a group of environmental contaminants that emanate from incomplete combustion of fuel or high temperature pyrolysis of fats and oils. It is well known that PAHs occur in curing smoke [5] and that they accumulate on fish products being smoked [6]. They have been extensively researched into because of their carcinogenicity and mutagenicity to animals [7]. In 2001, PAHs ranked 9th on the list of the most threatening compounds to human health [8].

Processing of fish for consumption mostly involve treatment of the fish with smoke. Smoking is a processing technique in which fish is exposed directly to wood smoke which may be generated by a variety of methods [9]. It has been found in literature that processing methods such as smoking can induce formation of PAHs in processed foods. Smoked products have traditionally received special attention because considerable amounts of PAH have been detected [10,11,12]. Several analyses of charcoal roasted common food items have proven the presence of PAHs such as benzo (a) pyrene, anthracene, chrysene, benzo (a) anthracene, indeno (1,2,3 -cd) pyrene [13,14]. Most of these PAHs have been found to be carcinogenic while some are not [2]. Several processing

techniques which includes: smoking, grilling and roasting, have been reported to induce formation of PAHs in foods. Of the various types of foods investigated, processed fish and meat products were found to contain high amount of PAHs [15]. Thus, the formation of PAHs during processing of foods poses a potential health hazard to humans. The US Environmental Protection Agency (EPA) and the European Union (EU) have PAHs on their list of priority organic pollutants owing to their ubiquitous nature of occurrence, recalcitrance, suspected carcinogenicity and mutagenicity. Polycyclic aromatic hydrocarbons are environmentally persistent due to their relative chemical stability and resistance to biodegradation. Reports have shown that exposure of human body to the environment containing PAHs may induce some fatal diseases such as lung and skin cancers [15].

A lot of data abound in literature on the effects of smoking on foods in developed countries of the world. However, in Nigeria, investigation of the consequences of methods of preparation of our foods on their nutritional composition appears to be at infancy, thus literature information on the relationship between methods and PAH content in processed food is scanty. In view of this, the study therefore sought to investigate the PAHs concentration in two types of smoked fish processed using firewood and charcoal which are generally consumed in every parts of Nigeria.

2. Materials and Methods

2.1. Collection of Fish Samples

Two species of locally consumed fresh fish in Nigeria namely: stock fish and cat fish, were used for this research. They were bought fresh from three sources, pooled together in Ogbomoso, Oyo State, Nigeria. Immediately, they were transported in ice chest to the laboratory of Chemistry Department of Pure and Applied Chemistry LAUTECH Ogbomoso. The fish were washed with tap water, identified using the fish identification key. The fish were weighed and the length taken using calibrated weighing balance and ruler. They were divided into two parts; one part homogenized using a 3 KV blender and dried in an oven for 48 hours at low temperature of about 40 °C. The second part was smoked.

2.2. Smoking Process

Samples were smoked using two processing methods such as: The fish were placed over wire gauze that is on burning firewood or charcoal. Duration of smoking of the fish ranged from 1 hour to 4 hours, while the smoking temperature ranged from 200 – 210 ^{o}C and a thermometer used to take the temperature of the smoking process. The smoked was produced by the burning of fire wood or charcoal. Wire gauze was placed on the burning fire wood/ charcoal, while the fish were placed over the wire gauze for 1h, 2h, 3h and 4h. The smoked fishes were further dried in an oven at low temperature of 40°C for 48 hours. The smoked dried fishes were then homogenised using a 3 KV blender, wrapped in aluminium foils paper to reduce microbial infestation and stored in a refrigerator at 4 °C before extraction and analysis were done.

Figure 1. Smoking of Fish

3. Proximate Analysis of Fish Samples

The proximate analysis involved repeated analysis of food to determine their nutrient quantity; it estimates moisture content, ash content, crude fiber, crude protein, fat and carbohydrate. It was carried out as described in the official method of the Association of Official Analytical Chemist [16].

4. Extraction of the Raw and Processed Fish Samples

Each of the samples was pulverized to ensure homogenization. Pulverized sample (10 g) was weighed into a test tube and extracted sequentially by ultrasonication for 20 minutes using 20 ml of methanol. Thereafter, the supernatant of the extract was decanted into a beaker and 20ml of fresh solvent added for another 20 minutes of ultrasonication. The process was repeated with another fresh solvent for 20 minutes. After this, a mixture of 20ml of methanol and dichloromethane ratio 1: 1 was added followed by ultrasonication for 20 minutes and the supernatant also decanted to the beaker containing the methanol extract, this was repeated twice. Furthermore, 20 ml of dichloromethane was added followed by 20 minutes of ultrasonication. This step was repeated twice and the supernatant decanted into the same beaker. The combined extract (180 ml) was then centrifuged at 2500 rpm for 10 mins and the supernatant decanted and filtered using whatman filter membrane. The solvent contained in the extract was evaporated using rotary evaporator, before the separation/clean up.

4.1. Clean up of Samples

The cleanup of the samples was performed with a silica/alumina column. Aliphatic fractions were eluted with n-hexane; the polycyclic aromatic hydrocarbons were eluted with a mixture of dichloromethane/n-hexane in ratio 3:2 while the free fatty acid (FFA) were eluted with methanol. The volume of the eluted fractions were

reduced to 1ml using rotary evaporator and kept in the refrigerator for GC/FID analysis.

4.2. GC-FID Determination of Polyaromatic Hydrocarbons (PAHs)

PAHs standard, 1000ppm (Catalog Number: H-MQME-01) containing 23 environmental PAHs components was purchased from AccuStandard. Five point serial dilution calibration standards (2.00, 4.00, 6.00, 8.00, 10.00ppm) was prepared from the stock and used to calibrate the GC-FID.

Determination of the levels of PAHs in the sample was carried out using GC-FID. Agilent 7890B gas chromatograph coupled to flame ionization detector (FID) was used. The stationary phase of separation of the compounds was HP-5 capillary column coated with 5 % Phenyl Methyl Siloxane (30m length × 0.32mm diameter × 0.25µm film thickness) (Agilent Technologies). 1µL of the samples were injected in splitless mode at an injection temperature of 300 ^{o}C, at a pressure of 13.74psi and a total flow of 21.364Ml/min. Purge flow to split vent was set at 15 mL/min at 0.75 min. Oven was initially programmed at 40 ^{o}C (1 min) then ramped at 12 ^{o}C/min to 300°C (10 min). FID temperature was 300 ^{o}C with Hydrogen: Air flow at 30 Ml/min: 300mL/min, Nitrogen was used as makeup gas at a flow of 22 mL/min. After calibration, the samples were analyzed and corresponding PAHs concentration obtained

5. Results and Discussion

The PAHs contents of firewood and charcoal smoked fishes are as contained in Table 1 and Table 2. 28 PAHs were found in the two species of fish samples which were smoked employing the traditional smoking methods with charcoal and firewood as the source of heat at a temperature range of 200 – 210 ^{o}C. From Table 1, which shows the results for firewood smoked stock fish (FSSF) and charcoal smoked stock fish (CSSF) at various time intervals. It was observed that naphthalene was below detection limit in FSSF 1h – 4h but was detected in CSSF samples. Pyrene was below detection limit in FSSF 1h, 3h and CSSF 3h, also, benzo (j) fluoranthene was below detection limit in FSSF 2h, CSSF 1h and 2h. Futhermore, dibenzo (a,i)pyrene was below detection limit in FSSF 2h, 3h and 4h. It was also observed that the concentration of various PAHs detected were higher in the charcoal smoked fish.

Table 1. PAH Profile for Firewood and Charcoal Smoked Stock Fish at Different Period of Smoking

PAHs	Concentration of PAHs in Samples (mg/kg)								
	UPSF	FSSF 1	FSSF 2	FSSF 3	FSSF 4	CSSF 1	CSSF 2	CSSF 3	CSSF 4
Na	Bdl	Bdl	Bdl	Bdl	Bdl	0.31	0.17	0.23	0.31
Acy	0.04	1.20	0.17	1.18	0.59	0.24	0.66	0.19	0.53
Ace	0.08	0.58	0.17	0.33	0.17	0.15	0.37	0.13	0.70
Fl	0.32	0.87	0.46	0.57	0.35	1.01	0.70	1.14	0.41
An	0.22	1.61	0.34	0.37	0.32	0.94	0.30	0.38	0.50
Ph	0.08	0.11	0.10	0.25	0.11	0.19	0.11	0.19	0.31
Flu	0.30	0.83	0.46	0.59	0.47	2.14	0.76	1.43	1.35
Pyr	0.01	Bdl	0.01	Bdl	0.47	0.15	0.07	Bdl	6.60
BcA	Bdl	0.02	0.09	0.01	0.04	0.02	0.08	0.47	33.29
Cry	0.22	0.26	0.27	0.25	0.26	0.38	0.25	0.33	0.35
BaA	0.12	0.26	0.19	0.22	0.20	1.65	0.32	1.72	8.23
BeP	0.26	1.12	0.59	0.04	0.66	1.01	0.24	2.87	9.68
Bbf	0.29	1.38	1.14	0.84	0.44	1.95	1.57	3.23	3.72
BaP	0.14	1.76	0.42	0.36	0.99	0.39	0.39	0.80	0.43
Bkf	0.02	0.21	0.19	0.24	0.23	0.36	1.37	0.36	0.24
Bjf	0.05	0.47	Bdl	1.45	0.14	Bdl	Bdl	0.74	3.29
7,12DBA	0.18	0.22	0.22	0.17	0.43	0.35	2.65	0.25	1.90
InP	0.09	0.28	0.28	4.04	0.28	2.67	0.69	205.92	27.91
3-MCl	0.34	0.86	0.67	0.60	0.65	2.48	3.60	0.63	10.83
DahA	0.21	0.79	0.62	3.56	0.58	Bdl	0.59	3.09	4.86
Bghip	0.28	0.51	0.49	0.92	0.47	1.25	0.40	4.97	6.44
Dalp	0.14	0.41	0.45	0.39	0.42	32.88	0.36	0.63	1.11
Daip	Bdl	0.29	Bdl	Bdl	Bdl	0.04	0.10	0.84	0.51
Dahp	0.12	0.36	Bdl	0.48	Bdl	5.44	Bdl	0.68	0.63
Total	3.51	13.39	7.36	16.84	8.25	1352.23	1388.63	1736.06	1614.33

Bdl = below detection limit
UPSF = unprocessed smoked fish, FSSF = firewood smoked stock fish, CSSF= charcoal smoked stock fish
Na = Napthalene, Acy = Acenaphthylene, Ace = Acenapthene, Fl = Fluorene, An = Anthracene, Ph = Phenanthrene, Flu = Fluoranthene, Pyr = Pyrene, BaA = Benzo(a)anthracene, BeP = Benzo(e)pyrene, BbF = Benzo(b)fluorene, BaP = Benzo(a)pyrene, BkF = Benzo(k)fluorene, BjF = Benzo(j)fluorene, 7,12-DBaA = 7,12-Dimethylben(a)anthracene, InP = Indeno(1,2,3-cd)Pyrene, 3-MCl = 3- Methyl chlolanthene, D(a,h)A = Diben(a,h)anthracene, BghiP = Benzo(g,h,i)perylene, DalP = Dibenzo(a,l)Pyrene, DaiP = Dibenzo(a,i)Pyrene, DahP = dibezo(a,h)Pyrene.

Table 2. PAH Profile for Firewood and Charcoal Smoked Cat Fish at Different Period of Smoking

PAHs	Concentration of PAHs in Samples (mg/kg)								
	UPCF	FSCF 1	FSCF 2	FSCF 3	FSCF 4	CSCF 1	CSCF 2	CSCF 3	CSCF 4
Na	0.21	0.24	0.39	3.03	8.07	0.96	4.49	Bdl	7.65
Acy	0.18	0.63	0.17	0.63	4.59	1.57	0.16	0.23	0.50
Ace	0.14	0.96	0.18	1.48	12.51	8.40	0.24	0.14	0.79
Fl	0.25	0.25	1.73	0.99	61.87	2.67	0.25	0.58	0.56
An	0.16	0.45	0.43	0.35	2.58	0.17	0.24	0.21	0.54
Ph	0.11	0.57	0.23	1.22	0.25	1.52	0.24	0.11	0.13
Flu	0.47	12.49	5.01	36.14	0.76	4.20	10.50	0.59	5.72
Pyr	6.25	39.01	23.82	11.53	1043.39	48.08	19.91	Bdl	57.15
BcA	3.39	24.54	6.18	114.38	84.64	74.28	28.78	12.77	98.04
Cry	0.24	110.12	25.23	0.26	15.97	46.41	1.59	0.29	2.60
BaA	0.20	4.50	1.99	0.47	3.65	0.43	0.23	0.21	4.13
Bep	0.22	15.82	3.78	5.07	3.56	0.20	0.92	0.24	16.68
Bbf	0.31	0.44	1.77	0.63	0.51	0.43	0.43	0.99	1.75
Bap	0.37	0.40	10.95	0.63	0.47	0.36	1.16	1.60	5.27
Bkf	0.23	13.50	0.33	0.45	0.32	0.19	0.20	0.78	0.32
Bjf	0.03	4.47	0.07	1.37	0.49	Bdl	Bdl	Bdl	Bdl
7,12-DBaA	0.21	0.50	1.32	0.18	0.28	1.51	0.20	0.25	0.17
Inp	0.26	2.25	0.35	0.27	0.35	1.44	1.29	0.33	0.32
3-MCl	0.35	1.69	0.91	0.35	0.48	4.14	0.67	2.88	0.58
DahA	0.52	2.15	1.36	0.57	0.60	0.83	0.99	2.25	0.60
Bghip	0.30	0.66	0.52	0.36	0.42	0.47	0.70	1.97	0.38
Dalp	0.32	3.03	0.51	0.39	0.36	0.36	0.91	0.42	0.40
Daip	0.12	6.09	3.37	1.31	0.22	0.85	0.02	0.05	1.28
Dahp	0.29	1.85	0.62	0.41	0.40	0.62	0.30	Bdl	0.53
Total	15.13	246.61	91.22	182.48	1248.77	200.11	1702.80	1657.11	1847.44

UPCF = unprocessed cat fish, FSCF = fire wood smoked cat fish, CSCF= charcoal smoked cat fish.

Table 3. Results of Proximate Composition of both the Stock Fish and Catfish Samples

	Proximate composition					
Samples	**%MC**	**%Ash**	**%CP**	**%Fat**	**%Fiber**	**%CHO**
UPSF	61.08	7.05	30.05	1.48	0.03	0.31
UPCF	63.51	5.64	25.60	5.21	0.00	0.60
FSSF 1h	60.34	7.89	30.44	1.05	0.00	0.28
FSSF 2h	58.91	7.07	32.17	1.14	0.01	0.70
FSSF 3h	46.67	7.69	41.37	2.17	0.02	2.07
FSSF 4h	41.99	5.75	47.71	2.14	0.01	2.37
CSSF 1h	57.83	5.03	32.00	1.11	0.00	4.03
CSSF 2h	38.13	3.45	54.27	3.19	0.01	0.93
CSSF 3h	12.67	2.68	63.33	5.35	0.00	15.97
CSSF 4h	9.35	3.01	65.92	6.00	0.00	15.72
FSCF 1h	63.26	5.59	25.35	5.13	0.00	0.67
FSCF 2h	58.22	6.11	26.43	8.42	0.00	0.82
FSCF 3h	32.72	7.69	31.19	20.17	0.00	8.23
FSCF 4h	15.73	10.55	35.81	28.17	0.00	9.74
CSCF 1h	46.91	4.39	40.23	7.99	0.00	0.48
CSCF 2h	42.83	4.15	39.00	13.05	0.00	0.97
CSFC 3h	38.01	4.20	37.18	20.18	0.00	0.43
CSFC 4h	31.47	4.22	32.00	25.71	0.00	6.60

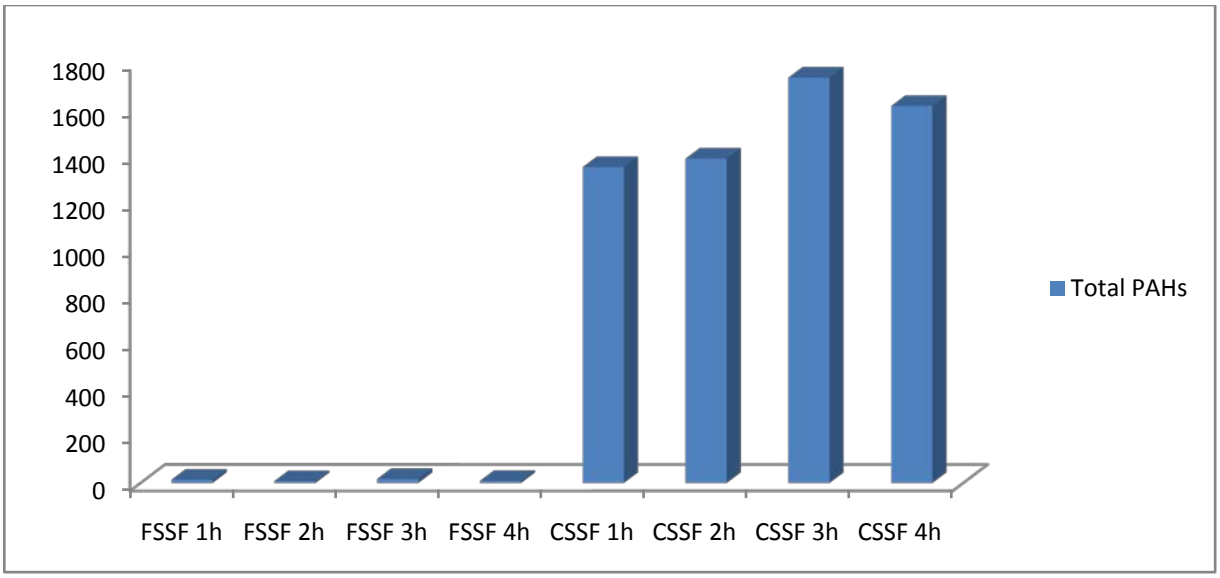

Figure 2a. Comparison of total PAHs profile in firewood smoked and charcoal smoked stock fish at time interval

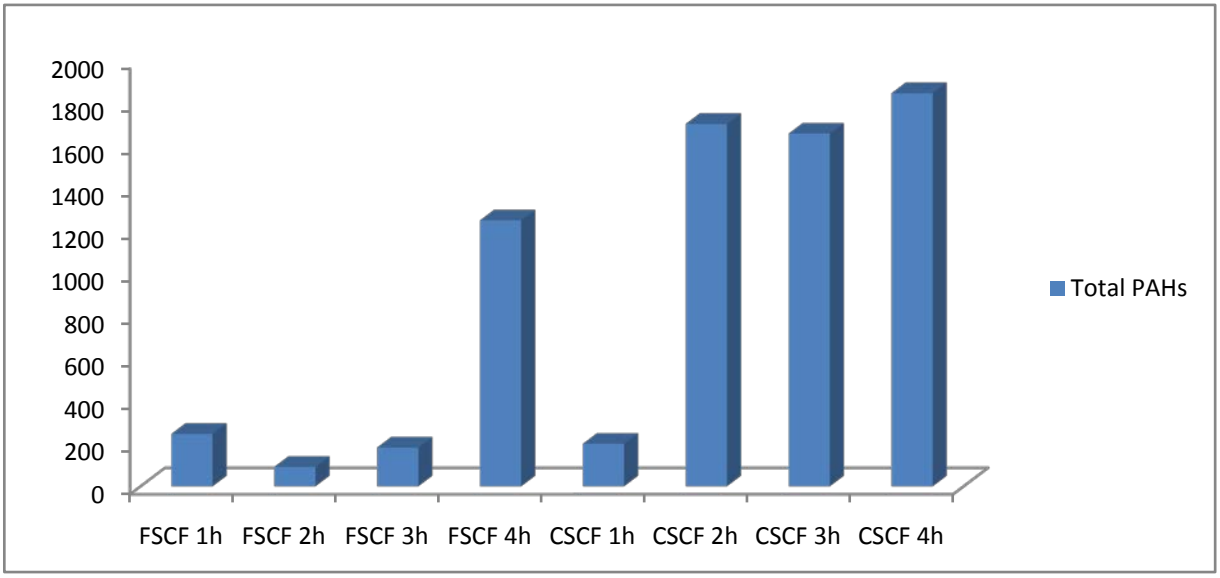

Figure 2b. Comparison of total PAHs profile in firewood smoked and charcoal smoked cat fish at time interval

The distribution of the total PAHs in FSSF and CSSF shows that the total PAH concentration levels in FSSF were lower (13.39, 7.36, 16.84 and 8.25 mg/kg for 1h, 2h, 3h, 4h respectively) than that of CSSF samples (1352.23, 1388.63, 1736.06 and 1614.33 mg/kg for 1h, 2h, 3h, 4h respectively). This could be ascribed to the high fat and protein content obtained for CSSF samples compared to the FSSF samples (Table 3). [17] Reported that there are strong correlations between fish lipids and PAH compounds; since PAH compounds are stored in fatty fish tissue. Pyrolysis of the fats in the fish generates PAHs that become deposited on the fish. PAH production by cooking over charcoal is a function of both the fat content in the fish and its proximity to the heat source [18,19].

Results of GC/FID for firewood smoked cat fish (FSCF) and charcoal smoked cat fish (CSCF) are shown in Table 2. All the priority PAHs were detected except in the samples CSCF 1h, 2h, 3h and 4h where benzo (j) fluoranthene was below detection limit, also, naphthalene and pyrene were not detectable in CSCF 3h. The total concentrations of PAH in firewood smoked stock fish were lower than the concentrations of PAHs for firewood smoked cat fish. This could be ascribed to the higher content of fat in the firewood smoked cat fish than in stock fish. Although the total concentrations of PAHs in charcoal smoked fish samples were generally higher, the concentrations of PAHs detected in the charcoal smoked cat fish were higher than those detected in charcoal smoked stock fish. All the high molecular weight PAHs except dibenzo (a,i)pyrene and dibenzo (a,h)pyrene were consistently present in much higher amount than other PAHs in all the samples of fish studied. This suggests there is higher resistance of these compounds to degradation [20]. Studies have shown that eating charcoal smoked food may expose one to the same quantity of PAHs as one would receive from smoking 600 sticks of cigarettes [21]. [22] and [19] carried out epidemiological studies which indicated a statistical correlation between the increased occurrence of cancer of the intestinal track

and frequent intake of smoked foods. The findings of this present study agree with [2] who reports that PAHs are common and may constitute health hazards in Nigeria. Since, stock fish and cat fish, smoked with firewood and charcoal, are popular delicacies for all classes of people in Nigeria, a precautionary steps need to be taken based on the health implications of the findings of this study.

The proximate analysis of the samples is as contained in Table 3. The moisture content of all the samples decreases steadily from 60.31 – 41.99 % in FSSF, 57.80 – 9.33 % in CSSF, 63.25 – 15.73 % in FSCF and 46.94 – 31.50 in CSCF. The crude protein contents of the samples shows a steady increase in all the samples except in CSCF where it shows a steady decrease. The crude protein content increases from 30.41 – 47.70 % in FSSF, 32.01 – 65.94 % in CSSF, 25.35 – 35.81 % in FSCF while the crude protein content decreases from 40.23 – 32.04 % in CSCF. The fat content shows an increase from 1.05 – 2.17 % in FSSF 1hr – 3hr but decreases again to 2.14 % in 4hr. In CSSF samples, the fat content increases from 1.11 – 6.00 %, also, there is increase in fat content from 5.13 – 28.17 % in FSCF, while the fat content increases from 7.99 – 25.71 % in CSCF.

The comparisons of firewood smoked stock fish with charcoal smoked stock fish at different time interval, and firewood smoked cat fish with charcoal smoked cat fish are presented in Figure 2 a and Figure 2 b below. It was observed that smoking of stock fish with firewood generally generates less PAH concentration as against smoking the same fish with charcoal. The PAH level was at highest concentration for charcoal smoked fish at 3rd hour of smoking Figure 2 a. From Figure 2b, the total PAH concentrations for firewood smoked cat fish is higher than what was observed in stock fish. The PAHs in fish increases as duration of smoking increases up to the 3rd hour, thereafter dropped at 4th Figure 2 a. For the charcoal smoked cat fish, the 4h smoking generated the highest concentration of PAH, the concentration of PAHs generated an increase from 1h to 2h smoking period, this then followed a steadily decrease to 3rd hour. The fact that concentrations of PAHs obtained for cat fish smoked with both firewood and charcoal were higher in all the samples with respect to stock fish processed under the same condition suggest that, the cat fish have specific adsorption property for PAHs when smoked [22]. Similarly, the total PAHs concentrations found in charcoal smoked stock fish was much higher than the concentration obtained for firewood smoked stock fish, which indicates that smoked fish using charcoal has higher adsorptive properties for PAHs than using firewood [22].

The source of PAHs was determined by molecular indices diagnostic ratio of some PAHs. The ratios obtained for stock fish and cat fish smoked at different time intervals, Table 4. The ratios of fluoranthene to pyrene, benzo (a) pyrene to chrysene and phenanthrene to anthracene were selected to predict the source of PAHs found in the fish samples. Ratios of fluoranthene to pyrene are greater than 1 suggesting that the PAHs found in the smoked fish were of pyrolytic source. Also, ratio of phenanthrene to anthracene less than 10 indicates combustion source and the ratio greater than 10 suggest petrogenic source [23]. The values obtained for these ratios were all less than 10 which suggests that the PAHs detected in all the samples were from combustion and pyrolytic sources. This implies that all PAHs found in the smoked fish were generated due to reactions initiated or aided by smoking temperature.

Table 4. Molecular Indices of PAHs in the Smoked Fish Samples

Sample	Phe/anth	BaP/cry	Nap/acen	Fluo/fluo + pyr
FSSF 1h	0.0675	6.7863	-	1.0000
FSSF 2h	0.30184	1.53709	-	0.98959
FSSF 3h	0.67308	1.44815	-	1.0000
FSSF 4h	0.33327	3.83319	-	0.43205
CSSF 1h	0.21172	1.04521	2.05344	0.86993
CSSF 2h	0.35709	1.53623	0.45220	0.90846
CSSF 3h	0.49527	2.46485	1.72911	1.0000
CSSF 4h	0.62282	1.22259	0.44614	0.05839
FSCF 1h	1.25946	0.00367	0.24750	0.00643
FSCF 2h	0.521909	0.43401	2.15563	0.06764
FSCF 3h	3.45089	2.45623	2.04680	0.07904
FSCF 4h	0.09646	0.02963	0.64555	0.05598
CSCF 1h	8.81518	0.00782	0.11452	0.05598
CSCF 2h	0.97568	0.73045	9.91877	0.01244
CSCF 3h	0.50673	2.07986	-	1.00000
CSCF 4h	0.24772	2.02931	9.69039	0.00975

Benzo(a)Pyrene toxicity equivalent concentration of smoked stock and cat fish

The benzo(a)Pyrene toxicity equivalent concentration in this study was used to determine the cancer potential of the smoked stock and cat fish and was calculated using the [24] model.

$$TEQ=\Sigma\left(PAH_i \times TEF_i\right)$$

Where PAH_i = concentration of individual carcinogenic polycyclic aromatic hydrocarbons, TEF = toxic equivalent factor (potency relative to benzo(a) pyrene) and TEQ = toxic equivalence

Cancer risk estimation formula by [24,25]

$$\text{Exposure Dose}=\frac{\text{concentration}\times\text{in take rate}\times\text{conversion factor}\times\text{exposure factor}}{\text{Weight of the Body}}$$

Where dose = estimated exposure dose, intake rate = 0.25 g of smoked fish, weight of the body = 65kg, conversion factor = (10^{-6}), exposure factor = (6times weekly = 312/365), concentration = concentration of total toxicity equivalent of Benzo (a) pyrene.

$$\text{Cancer Risk Estimation}=\frac{\text{Exposure dose}\times\text{number of years of eating smoked fish}\times\text{CPF}}{\text{Average life time}}$$

Where CPF = cancer potency factor and its (7.3) for Benzo (a) pyrene, number of years of eating smoked fish = assumed to be 30 years and average lifetime = 55 years,

Table 5a. Toxicity Equivalent Quotient (TEQ) of Benzo (A) Pyrene Concentration (Mg/Kg)

	TEQ FOR CARCINOGENIC PAHs						
Sample	BaA	Cry	BaP	Bb+kF	DahA	InP	Total Bap TEQ
TEF	0.1	0.01	1	0.1	1	0.1	
FSSF1	0.03	0.00	1.76	0.16	0.79	0.03	2.74
FSSF2	0.20	0.27	0.42	0.13	0.62	0.03	1.67
FSSF3	0.02	0.00	0.36	0.06	3.56	0.40	4.40
FSSF4	0.02	0.00	0.99	0.07	0.58	0.03	1.69
CSSF1	0.17	0.00	0.39	0.23	-	0.27	1.06
CSSF2	0.03	0.00	0.39	0.29	0.59	0.07	1.37
CSSF3	0.17	0.00	0.80	0.36	3.09	20.59	25.01
CSSF4	0.82	0.00	0.43	0.40	4.85	2.79	9.29
FSCF1	0.45	1.10	0.40	1.39	2.15	0.23	5.72
FSCF2	0.20	0.25	10.95	0.21	1.36	0.03	13.00
FSCF3	0.05	0.00	0.63	0.11	0.57	0.03	1.39
FSCF4	0.37	0.16	0.47	0.08	0.60	0.04	1.72
CSCF1	0.04	0.46	0.36	0.06	0.83	0.14	1.89
CSCF2	0.02	0.02	1.16	0.06	0.99	0.13	2.38
CSCF3	0.02	0.00	1.60	0.18	2.25	0.03	4.08
CSCF4	0.41	0.03	5.27	0.21	0.60	0.03	6.55

TEF: Toxic equivalency factor with respect to Benzo (a) pyrene from (Larsen and Larsen, 1998).

Table 5b. Daily Exposure Dose of Carcinogenic PAHs and Cancer Risk due to Exposure to Smoked Fish Samples

Sample	Exposure dose	Cancer risk estimation
FSSF1	9.01×10^{-8}	3.59×10^{-7}
FSSF2	5.49×10^{-8}	2.19×10^{-7}
FSSF3	1.45×10^{-7}	5.77×10^{-7}
FSSF4	5.56×10^{-8}	2.21×10^{-7}
CSSF1	3.49×10^{-8}	1.39×10^{-7}
CSSF2	4.51×10^{-8}	1.80×10^{-7}
CSSF3	8.22×10^{-7}	3.27×10^{-6}
CSSF4	3.06×10^{-7}	1.22×10^{-6}
FSCF1	1.88×10^{-7}	7.49×10^{-7}
FSCF2	4.28×10^{-7}	1.70×10^{-6}
FSCF3	4.57×10^{-8}	1.82×10^{-7}
FSCF4	5.66×10^{-8}	2.25×10^{-7}
CSCF1	6.22×10^{-8}	2.48×10^{-7}
CSCF2	7.83×10^{-8}	3.12×10^{-7}
CSCF3	1.34×10^{-7}	5.34×10^{-7}
CSCF4	2.15×10^{-7}	8.56×10^{-7}

The daily exposure dose of carcinogenic PAHs and cancer risk due to exposure to smoked stock and cat fish at different time duration were calculated as shown in Table 5a and Table 5b above. The exposure dose for FSSF and CSSF 1 – 4 hour ranged from $9.01 \times 10^{-8} – 1.45 \times 10^{-7}$ and $4.51 \times 10^{-8} – 3.06 \times 10^{-7}$ respectively. While, the exposure dose for FSCF and CSCF ranged from $5.66 \times 10^{-8} – 1.88 \times 10^{-7}$ and $7.83 \times 10^{-8} – 1.34 \times 10^{-7}$ respectively. The exposure doses for all the samples were lower than the maximum permissible exposure dose of 1×10^{-4}. The cancer risk estimation for samples FSSF and CSSF 1 – 4 hour ranged from $5.77 \times 10^{-7} – 2.19 \times 10^{-7}$ and $3.27 \times 10^{-6} – 1.22 \times 10^{-6}$ respectively. Though these values were lower than the permissible limit of 1×10^{-6} except the value for CSSF4 (1.22×10^{-6}) which is very close to the permissible limit. Also, cancer risk estimation for FSCF and CSCF 1 – 4 hour ranged from $7.49 \times 10^{-7} – 1.70 \times 10^{-6}$ and $8.56 \times 10^{-7} – 2.48 \times 10^{-7}$ respectively. All these values were lower than the permissible limit.

6. Conclusion

The diagnostic ratio calculated to predict the source of polycyclic aromatic hydrocarbons in the smoked fishes in this research showed that the PAHs generated were from pyrolytic source. The quantity of PAHs profiles for the stock fish and cat fish smoked using fire wood and charcoal reveals that the total concentration of PAHs in smoked cat fish is higher than in smoked stock fish. Nevertheless, the type of source of fuel used in the smoking of the two species of the fishes impacted greatly on the PAHs profiles of the smoked fishes. Also, the study shows that duration of smoking is very important variable in the PAHs content of charcoal and fire wood smoked fishes. The high content of PAHs found in charcoal smoked fishes may be due to the fact that charcoal is made from agglomerate of different woods.

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