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COMPARATIVE DRYING PROFILES AND POLYCYCLIC AROMATIC HYDROCARBON CONTENT OF CATFISH SMOKE-DRIED USING TRADITIONAL DRUM AND NEWLY CONSTRUCTED ECO FISH KILN

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ABSTRACT

Smoke-drying is the most popular processing technology utilized in increasing the shelf-life of fresh fish in nigeria. the deposit of polycyclic aromatic hydrocarbons (pahs) on the fish during smoke-drying process however has potential health implications when consumed. this study investigated the drying profiles and levels of pahs in catfish (clarias gariepinus) samples smoke-dried using traditional drum kiln (tdk) and a newly constructed ecologically friendly fish kiln (efk) fitted with different sizes of smoke filters (0.1 cm in two layers, 0.3 cm in two layers and 0.3 cm in four layers). the drying profile was obtained by plotting the average weight and moisture loss of the smoke-drying catfish against time while the extraction method for pah samples was conducted according to american society for testing and materials astm d3328 and astm 3415 methods. the results showed that the drying profile of efk fitted with 0.3cm smoke filter in two layers gave the best output on the quality of drying in terms of percentage weight loss over time. levels of benzo(a)pyrene and pah4 [benzo(a)pyrene, benzo(a)anthracene, benzo(b)fluoranthene and chrysene] of smoke-dried catfish using tdk were higher than levels using efk fitted with 0.1 and 0.3 cm smoke filters although all were lower than maximum european union level of 0.005 and 0.03 mg/kg respectively. the study showed that maintaining temperatures between 60 - 80^0 c produced smoke-dried catfish products considered safe for human consumption when both kilns were used with best results from efk fitted with two layers of o.3 cm smoke filters.

KEY WORDS: *Catfish, Pah, Eco Fish Kiln, Traditional Drying Kiln*

INTRODUCTION

Fish forms part of the most basic diet for many people all over the world and is known to have high nutritional values (Kromhout *et al*., 1995; Steffens, 2006; Fawole *et al*., 2007). Nigeria is a nation with a teeming population of about 170 million people and has fish demand estimate of 2.1 million metric tons per annum having a domestic production of about 900,000 metric tons and a deficit bridged mostly by importation (Adekoya and Miller, 2004; World Bank, 2012; NBS, 2013). Aquaculture is encouraged to discourage importation and improve the Nigerian economy. The deliberate production of fish as an economic resource by a large number of people especially small-scale farmers in Nigeria (Davies *et al.,* 2008). The most successful fish species cultured in Nigeria is catfish (Oladejo, 2010) because of its ability to thrive under stressful conditions such as low oxygen concentrations and high feed to muscle conversion ratio (Agbede *et al*., 2003).

Daily consumption or sale of freshly harvested fish is not always possible hence the need to delay the inevitable natural deterioration process and extend the shelf life of the freshly harvested fish in order to prevent wastage. This can be done using preservative or processing methods (Okonta and Ekelemu, 2005; Obodai *et al.,* 2009). The oldest and most widely practiced form of fish processing particularly in Nigeria is smoke-drying as it is favoured over preservation methods such as freezing because of the epileptic power supply, high costs of maintaining generators, easy access to raw materials required for smoke-drying and the unique flavour smoke-dried fish has which makes it a delicacy in Nigeria (Eyo, 2001 and Olokor *et al.,* 2007).

Smoke-drying is usually carried out in smoke houses, smoking ovens or smoking kilns with designs which vary from place to place. The most popular smoking kiln in Nigeria is the Traditional Drum Kiln because of its ease of use, low cost, easy procurement with the fish dried using combination of smoke and heat generated from wood sources such as firewood, charcoal or sawdust. Challenges faced with the use of Traditional Drum Kiln include the direct location of the heat source under the smoke-drying fish and the subjective control of the amount of heat and smoke which smoke-dries the fish product leading to a lack of standardization of the smoke-dried fish product (Abolagba and Nuntah, 2011). The direct dripping of the oil from the fish being processed (by smoke-drying) unto the smoldering fuel breaks down the oil. This can lead to fire outbreak and excessive smoke generation which directly coats the fish. Smoke contains Polycyclic Aromatic Hydrocarbons (PAHs) also known as the Poly Nuclear Aromatic Hydrocarbons which are formed as a result of incomplete combustion or thermal decomposition of organic materials such as wood (FAOWHO, 2006). This smoke contains compounds such as phenolic, carboxyl and some poly aromatic hydrocarbons such as benzopyrene which are suspected to have (negative health implications such as) hematological, immunological and carcinogenic effects at high concentrations and can thus have serious health implications with constant consumption (Nisbet and Lagoy, 1992; Eyo, 2001; Ako and Salihu, 2004; Ramesh *et al.,* 2004; Lin *et al.,* 2008).

The aim of this study was to design and construct a new smoke-drying kiln with different smoke filters, standardize the existing Traditional Drum Kiln and compare the drying profiles and Polycyclic Aromatic Hydrocarbons (PAHs) deposit on catfish smoke-dried using both traditional drum kiln (TDK) and new kiln (EFK) fitted with different sizes of smoke filters.

MATERIALS AND METHODS

Both TDK and EFK used for this study were constructed and assembled at the Instrumentation Unit of the Department of Physics, University of Lagos.

Construction of Traditional Drum Kiln (TDK)

The traditional smoking kiln was constructed using a cylindrical metal drum as used in sampled fishing villages where fish processing is done by smoke-drying. The metal drum had dimensions of 72 cm height, 187 cm circumference and 55 cm diameter opening at the top. A circular opening of diameter 36 cm was carved out at the bottom and served as the vent where heat was applied. A circular wire rack with a diameter of 76.5 cm was placed on top of the traditional drum and served as the fish drying tray on which the fresh catfish was arranged for the smoke-drying process. The assembled kiln was placed on a flat rectangular iron base with dimensions 106 cm length, 57.2 cm width and 1.8 cm height for the smoke-drying process. The fully assembled traditional drum kiln is presented in Plate 1.

Plate 1: Fully Assembled Traditional Drum Kiln

Construction of Eco Fish Kiln (EFK)

The Eco Fish kiln (EFK) was built with a carrying capacity of about 20 kg. Two smoke filters with diameters 0.1 cm and 0.3 cm (Plates 2a and b) were used in three combinations for this study (0.1 cm wire mesh smoke filter in two layers, 0.3 cm wire mesh smoke filters in two layers and 0.3 wire mesh smoke filters in four layers). The EFK is consisted of three parts; the drying chamber, the flame chamber and the electronics.

Plate 2a: 0.1cm Smoke Filter Used in EFK

Plate 2b: 0.3cm Smoke Filter Used in EFK

The Drying Chamber**:** The drying chamber was constructed by fortifying a metal iron mesh with lagging material (refractory) made up of a composite mixture of clay, sawdust and silicon carbide in the ratio 4:2:0.5. A fish drying stand with three layers was placed in the drying chamber for smoke-drying and a smoke outlet made out of a cylindrical rod of 18.9 cm length and 8.4 cm diameter was built on the side away from the smoke-processor. The drying chamber was fitted with a parabolic dome shaped cover of diameter 68 cm with the convex side facing the inside. The outer side of the cover and the body of the drying chamber was covered with a thick paste of lagging material, cemented and allowed to dry naturally before use.

The Flame Chamber: The flame chamber was constructed by arranging red bricks in a staggered manner to give room for expansion during smoke-drying. Fortification was done with four iron rods with dimensions 93.2 cm length and 4.5 cm diameter inserted at the four corners of the flame chamber. The brick walls were coated on the inside and outside with the refractory material to seal in most of the heat generated from the heat source and allowed to dry naturally before being cemented to prevent the lagging material from easily eroding. An aperture with dimensions 29.6 cm length and 16.8 cm breadth was made at the front to serve as inlet for firewood used as source of fuel. Smoke filter layers were placed at the back where the flame chamber joined with the drying chamber. The fully assembled flame chamber had dimensions of 93.1 cm length, 77.5 cm breadth and 85.2 cm height. A flat iron plate 78.4 cm in length and 56.6 cm in breadth was placed on the flame chamber and twenty-one refractory bricks each with dimensions 23.4 cm length, 11.3 cm breadth and 5.1 cm height were placed on the flat iron plate placed on the flame chamber to contain the heat generated from the heat source. **Plate 3** shows a full picture of the Eco Fish kiln (EFK) as used for this study.

Plate 3: Constructed Eco Fish Kiln (EFK)

The Electronic Components: The electronics of the Eco Fish kiln (EFK) entailed the building of an electronic control system to guide in the maintenance of optimum temperature range of 60 -85^0 C within the drying chamber (Clucas, 1990). The electronics for this study composed of temperature sensor built as a small metal nub that transferred heat to an audio alarm to indicate no noise, a beeping sound or gave a loud alarm at less than 60, 60 - 80 and above 85^0 C respectively. Visual Light Emitting Diode (LED) indicators were powered by one 9V battery and consisted of red, blue and green lights which stayed off, blinked with a second interval or stayed on according to temperature range.

The following parameters were measured during the smoke-drying process: average smoke-drying temperature on an hourly basis, weight loss on an hourly basis, percentage weight loss during smoke-drying, the drying profile of each smoke-drying kiln and the PAH levels of the smoke-dried catfish product.

Sample Collection, Preparation and Smoke-drying Process: *Clarias gariepinus* were obtained live from the Aquaculture Unit of the Department of Marine Sciences, University of Lagos, stunned with a wooden club, washed with clean pipe borne water and then arranged on covered metal racks to air dry. No seasoning or oil was applied to the fresh samples before being arranged in TDK and EFK. The smoke-drying process using both kilns was carried out at a stretch lasting an average of 24 ± 3 hours at a temperature range of 60 - 85^0 C, maintained with the aid of temperature alarm and Visual Light Emitting Diode. The fish were measured on an hourly basis till a fairly constant weight was achieved.

Drying Profile Determination: The drying profiles of Traditional Drum Kiln (TDK) and Eco Fish Kiln (EFK) were calculated by plotting the average weights of the smoke-dried catfish in both kilns against time at hourly intervals.

Polycyclic Aromatic Hydrocarbons (PAHs) Determination: The extraction method for the analysis of poly aromatic hydrocarbons profiles in the smoke-dried fish samples were followed by employing the modified methods of American Society for Testing and Materials ASTM 3328 and ASTM 3415. Fifty grams of smoke-dried catfish sample was crushed in a mortar with a pestle. The crushed sample was placed in flat borosilicate container and dried in the oven at 60^0 C (AOAC, 2006). Twenty grams of the dried sample was weighed into a 250 ml capacity beaker of borosilicate material for fat extraction, esterified and the seterifiable fat was removed by soxhlet extraction. The aliphatic and polyaromatic hydrocarbons were extracted with 100ml of the ratio 3;1 redistilled hexane: dichloromethane in the beaker. The beaker and its contents were placed in the sonicator to extract the hydrocarbon for about two hours. The organic layer was filtered into the 250 ml capacity borosilicate beaker. The extract was dried by passing the filtrate through the funnel containing the anhydrous sodium sulphate. The dried extract was concentrated with a stream of nitrogen gas.

The concentrated oil was then separated into the aliphatic profiles and poly aromatic hydrocarbons profiles by packing the glass column with activated alumina, neutral and activity grade 1. Ten ml of the treated alumina was packed into the column and cleaned properly with redistilled hexane. The extract was poured onto the alumina and was allowed to run down with the aid of the redistilled hexane to remove the aliphatic profiles into a pre cleaned 20ml capacity glass container. The aromatic fraction was recovered by allowing the mixture of hexane and dichloromethane in ratio 3 to 1 and removing the most polar PAH by removing the dichloromethane into the precleaned borosilicate beaker. The mixture was concentrted to 1.0ml by stream of the nitrogen gas before the gas chromatography analysis (EFSA, 2008). This was used to test the levels of PAH in smoke-dried catfish in traditional drum kiln and in Eco Fish kiln with different sizes and combination of mesh sizes namely 0.1cm in two layers, 0.3 cm in two layers and 0.3cm in four layers.

Statistical Analysis

All data are presented as means ± standard error (SE). Analysis of variance (ANOVA) was set at 0.05 level of significance and T-test were carried out using Excel, PAST 3 and SPSS 20.0 software.

RESULTS

Drying Profiles and Weight Loss of *Clarias Gariepinus* Smoke-Dried using Traditional Drum and Eco Fish Kiln Fitted with Two Layers of 0.1 cm Smoke-Filters, Two Layers of 0.3cm Smoke Filters and Four Layers of 0.3 cm Smoke Filters

The initial weights of the fresh catfish prior to smoke-drying and final weights after smoke-drying were averaged at 271.00 g, 228.80 g, 219.86 g and 219.50 g and 95.00 g, 74.35 g, 69.51 g and 51.76 g using Traditional Drum Kiln (TDK) and Eco Fish Kiln fitted with two layers of 0.1cm smoke filter, two layers of 0.3cm smoke filter and four layers of 0.3cm smoke filter respectively as shown in Figures 1 and 2. Most rapid weight loss of an average of 50% was in the first five (5) hours using both kilns. The smoke-drying process however had to be stopped at eighteen hours using TDK as the catfish samples had become very brittle and were starting to disintegrate. The highest clogging of the smoke filters was found with EFK using combination of two layers of 0.1cm smoke filters and the least clogging was found in EFK using combination of two layers of 0.3cm smoke filters.

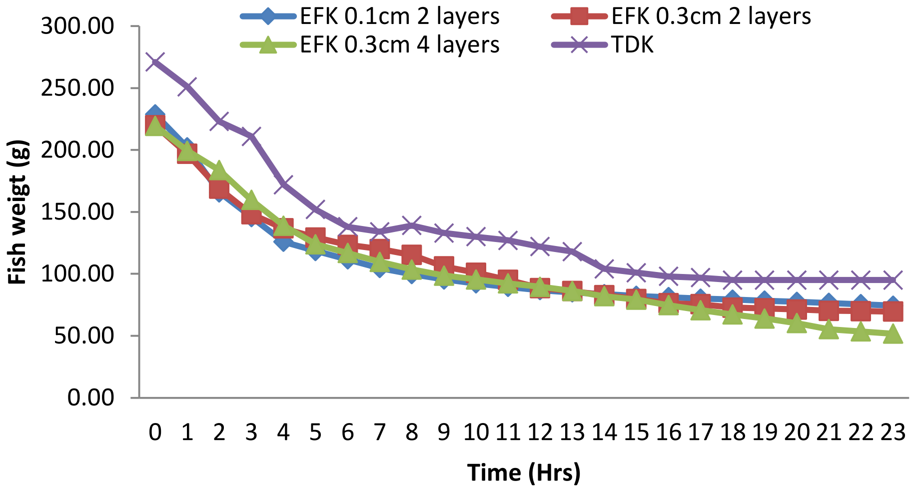

Figure 1: Fish Weight of the Smoke-dried Catfish Samples using Eco-Friendly and Traditional Smoke-drying Kilns

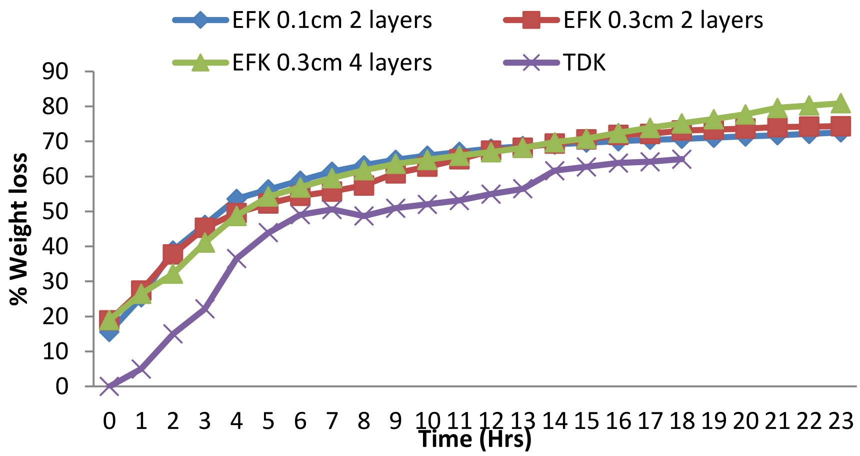

Figure 2: Percentage Weight Loss of the Smoke-dried Catfish Samples using Eco-Friendly and Traditional Smoke-drying Kilns

Polycyclic Aromatic Hydrocarbon (PAHs) Content on *Clarias Gariepinus* Smoke-Dried using Traditional Drum and Eco Fish Kiln Fitted with Two Layers of 0.1 cm Smoke-Filters, Two Layers of 0.3cm Smoke Filters and Four Layers of 0.3 cm Smoke Filters

Poly Aromatic Hydrocarbons in *Clarias gariepinus* smoke-dried using Traditional Drum Kiln (TDK) and Eco Fish Kiln (EFK) fitted with varying combinations of smoke filters were namely Pyrene, Phenanthrene, Naphthalene, Indeno (1,2,3-cd) pyrene, Fluorene, Fluoranthene, Dibenzo (a,h) anthracene, Chrysene, Benzo (k) fluoranthene, Benzo (g,h,i) perylene, Benzo (b) fluoranthene, Benzo (a) pyrene, Benzo (a) anthracene, Anthracene, Acenaphthylene and Acenaphtene as shown in Table 1. The highest total PAH value was observed to be 0.012 mg/kg in catfish smoke-dried using Traditional Drum Kiln while the lowest value was found to be 0.0093 mg/kg in catfish samples smoke-dried using Eco Fish Kiln fitted with two layers of 0.3 cm smoke filters. Benzo (a) pyrene concentrations in the smoke-dried damples are as shown in Table 2 to be highest in samples processed using TDK (0.000264 mg/kg) and lowest in samples smoke-dried using EFK fitted with two layers of 0.3 cm smoke filter (0.000218 mg/kg) while PAH4 Benzo (a) pyrene , Benzo (a) anthracene, Benzo (b) fluoranthene and Chrysene as measured by Scientific Panel on Contaminants in Food Chain (CONTAM PANEL) (EFSA, 2008) were found to be highest with samples processed using TDK (0.00475 mg/kg) and lowest in samples smoke-dried using EFK fitted with two layers of 0.3 cm smoke filters (0.000370 mg/kg) (Table 2).

Table 1: PAH Content in Smoke-dried *Clarias gariepinus* Smoke-dried Using Traditional Drum and Eco-Friendly Kilns

Poly Aromatic Hydrocarbon	Traditional Drum Kiln (mg/kg)	Eco-Friendly Kiln with Two Layers 0.1 cm Smoke Filter (mg/kg)	Eco-Friendly Kiln with Two Layers 0.3 cm Smoke Filter (mg/kg)	Eco-Friendly Kiln with Four Layers 0.3cm Smoke Filter (mg/kg)
Naphthalene	0.0005 ± 0.000069[bc]	0.00034 ± 0.000069[cd]	0.00023 ± 0.000069[ab]	0.00031 ± 0.000069[bc]
Acenaphthylene	0.00031 ± 0.000069[bc]	0.00013 ± 0.000069[ab]	0.00013 ± 0.000069[ab]	0.00012 ± 0.000069[bc]
Acenaphtene	0.00049 ± 0.000069[cd]	0.00047 ± 0.000069[cd]	0.00050 ± 0.000069[bc]	0.00046 ± 0.000069[cd]
Fluorene	0.00061 ± 0.000069[de]	0.00059 ± 0.000069[a]	0.00058 ± 0.000069[ab]	0.00059 ± 0.000069[bc]
Phenanthrene	0.0016 ± 0.000069[cd]	0.0013 ± 0.000069[f]	0.00021 ± 0.000069[ab]	0.0012 ± 0.000069[b]
Anthracene	0.00102 ± 0.000069[f]	0.00089 ± 0.000069[f]	0.00081 ± 0.000069[bc]	0.00081 ± 0.000069[d]
Fluoranthene	0.0062 ± 0.000069[f]	0.0033 ± 0.000069[f]	0.0044 ± 0.000069[ab]	0.0047 ± 0.000069[e]
Pyrene	0.00077 ± 0.000069[e]	0.0019 ± 0.000069[f]	0.0019 ± 0.000069[cd]	0.0019 ± 0.000069[d]
Benzo (a) Anthracene	0.00013 ± 0.000069[ab]	0.00012 ± 0.000069[ab]	0.00011 ± 0.000069[ab]	0.00012 ± 0.000069[cd]
Chrysene	0.000035 ± 0.000064[a]	0.000023 ± 0.000064[a]	0.000024 ± 0.000064 [a]	0.000022 ± 0.000064[e]
Benzo (b) Fluoranthene	0.000038 ± 0.000064[a]	0.000032 ± 0.000064 [a]	0.000017 ± 0.000064 [a]	0.000034 ± 0.000064[a]
Benzo (k) Fluoranthene	0.000034 ± 0.000064[a]	0.000034 ± 0.000064 [a]	0.000039 ± 0.000064[ab]	0.000034 ± 0.000064[a]
Benzo (a) Pyrene	0.00026 ± 0.000064[bc]	0.00023 ± 0.000064 [a]	0.00022 ± 0.000064[de]	0.00023 ± 0.000064[bc]
Indeno (1,2,3-cd) Pyrene	0.0000095 ± 0.000064[a]	0.0000088 ± 0.000064 [a]	0.0000089 ± 0.000064 [a]	0.0000084 ± 0.000064[a]
Dibenzo (a,h) Anthracene	0.000076 ± 0.000064[a]	0.000043 ± 0.000064 [a]	0.000077 ± 0.000064[f]	0.00005 ± 0.000064[a]
Benzo (g,h,i) Perylene	0.000019 ± 0.000064[a]	0.000012 ± 0.000064 [a]	0.000024 ± 0.000064 [a]	0.000015 ± 0.00006[a]
TOTALS	**0.012 ± 0.00021**	**0.0094 ± 0.00013**	**0.0093 ± 0.00016**	**0.011 ± 0.00017**

Mean ± S.E (standard errors) of each PAH using TDK and EFK with the same alphabet(s) in the same column are not significantly different ($p > 0.05$)
TDK: Traditional Drum Kiln
EFK: Eco-Friendly Kiln

Table 2: Benzo(a)pyrene PAH 4 Summation (mg/kg) in Catfish Smoke-dried with Traditional Drum Kiln (TDK) and Eco Fish Kiln (EFK) with 0.1 and 0.3 cm Smoke Filter Mesh Sizes

Smoking Kilns	B[a]P	B[a]A	B[b]F	CHR	PAH 4 Summation
TDK	0.000264	0.000138	0.000038	0.000035	0.000475
EFK 2 LAYERS 0.1 cm (A)	0.000228	0.000119	0.000032	0.000023	0.000402
EFK 2 LAYERS 0.3 cm (B)	0.000218	0.000111	0.000017	0.000024	0.000370
EFK 4 LAYERS 0.3 cm (C)	0.000230	0.000121	0.000034	0.000022	0.000407

B[a]P: benzo[a]pyrene ; B[a]A: benzo[a]anthracene; B[b]F: benzo[b]fluoranthene ; CHR:Chrysene; TDK: Traditional Drum Kiln; EFK: Eco Fish Kiln

DISCUSSION

The rate of spoilage of freshly harvested fish in Nigeria is about 60 % due to factors such as prevailing high temperatures and poor available infrastructure for preservation and/or processing (Saliu, 2008). The drying profiles of TDK and EFK fitted with 0.1 cm smoke filters in two layers, 0.3 cm smoke filters in two layers and 0.3 cm smoke filters in four layers showed a general rapid loss of moisture in the first six hours which tapered off as the time progressed. EFK with the use of 0.1 cm smoke filters in two layers showed the poorest drying profile and could be attributed to the smoke filters being highly clogged by smoke particles and so prevented easy passage of heat to the smoke-drying fish. EFK fitted with 0.3 cm smoke filter in two layers showed the best drying profile as there was a gentle curve showing the continued weight loss of the smoke-drying catfish samples. This could be because the smoke filters had larger holes that allowed more smoke particles pass through and so prevented heavy clogging.

The incomplete combustion of organic materials when wood fuels are burned to smoke-dry fish coats the fish with Poly Aromatic Hydrocarbons (PAHs) which increases according to the closeness of the smoke-drying fish to the source of heat and smoke (Duke and Albert, 2007; Olabemiwo *et al*., 2011). Continual heavy consumption of PAHs have been shown to have negative health implications on humans (WHO, 2006; Amos-Tautua *et al.,* 2013).The European Union in 2005 and 2008 established the maximum limit for PAHs in food which include fish to be a maximum of 0.005 mg/kg as measured by only Benzo(a)pyrene [B(a)P]. This has however been reviewed by Scientific Panel on Contaminants in the food chain

(CONTAM Panel) to be four (4) PAHs namely benzo(a)anthracene [B(a)A], benzo(b)fluoranthene [B(b)F], benzo(a)pyrene [B(a)P] and chrysene as better indicators of PAH and stated a maximum summation value of 0.03 mg/kg. The results of the PAH Benzo(a)pyrene and PAH4 benzo(a)anthracene [B(a)A], benzo(b)fluoranthene [B(b)F], benzo(a)pyrene [B(a)P] and chrysene from the smoke-dried catfish samples from standardized TDK and EFK were all lower than EU standards with the lowest values found in catfish smoke-dried using EFK fitted with 0.3 cm smoke filter in two layers as 0.000230 and 0.000407 mg/kg respectively. The general lower values from both kilns can be attributed to the standardization by maintaining optimum drying temperature between 60 - 85^0 C (Clucas, 1990) while the lowest results in catfish samples smoke-dried using EFK with two layers of 0.3 cm smoke filters can be attributed to the minimal clogging of the smoke filters by smoke particles generated from the burning fuel.

CONCLUSION

Most of the fish harvested in the tropics is usually for direct consumption and a significant quantity of freshly harvested fish is lost as a result of inadequate technology to prevent post harvest losses. Standardizing the traditional drum kiln and new Eco Fish Kiln fitted with different smoke filters to optimal temperatures of 60 - 85^0 C and assessing the level of Polycyclic Aromatic Hydrocarbon deposits on smoke-died catfish has been able to show that the manner of smoke-drying in terms of temperature regulation and degree of exposure to smoke particles influences the drying rate as well as the accumulation of PAHs in the smoke-dried fish products.

The lower concentrations of PAH and PAH4 obtained from smoke-dried catfish samples using Traditional Drum Kiln and Eco Fish Kiln than European standards show that maintaining optimal temperatures of 60 - 80^0 C is ideal for smoke drying in order to produce smoke-dried fish acceptable for human consumption. EFK fitted with two layers of 0.3 cm smoke filters produced smoke-dried catfish samples with lowest Polycyclic Aromatic Hydrocarbon concentrations and also showed best drying profile and should thus be employed in communitues where smoke-drying is carried out to ensure good quality smoke-dried catfish to the Nigerian populace.

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