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Preservative Synergy of Phenol from *Tectonia grandis* and Some Indigenous Preservatives on Smoked *Clarias gariepinus*

KESTER, CT

Department of Biological Sciences, Bells University of Technology, Ota, Ogun State, Nigeria

***Email:** christieradeke@gmail.com; tckester@bellsuniversity.edu.ng*
***Tel:** +2348030688435*

ABSTRACT: The preservation potentials of phenol produced by hardwood, *Tectonia grandis* and some selected indigenous preservatives on smoked *Clarias gariepinus* were investigated in this study. A sample size of 168 catfish was pre-treated with single (10.0% salt (FS), 10.0% lime (FLM), 10.0% pepper (FPP),) and combined (5.0% salt and 5.0% lime (FSL), 5.0% salt and 5.0% pepper (FSP), 5.0% lime and 5.0% pepper (FLP), 3.3% salt, 3.3% lime and 3.3% pepper (FSLP)), untreated serving as control. The fish samples were smoked at 90.0±5.0ºC for 16 hours, stored under ambient conditions for twelve weeks. Phenol (mg/kg) and Total volatile base-Nitrogen (TVB-N, mgN/100g) were determined at 0, 2, 4, 6, 8, 10 and 12 weeks using official methods of analysis of the Association of Official Analytical Chemist. Phenol levels ranged from 1.21±0.01 to 1.31±0.00 mg/kg in untreated samples and 1.16±0.00 (FS) to 1.33 ±0.00 (FLM). Mean values of Total Volatile Bases in Nitrogen (TVB-N) were significantly different ($p<0.05$), ranging from 14.24±0.02 to 31.38±0.03mgN/100g in untreated samples and 11.06±0.03 (FS) to 128.60±0.04 mgN/100g (FPP) in treated. The use of pepper as single preservative on smoked fish should be avoided as it must have promoted autolytic process which led to the formation of high level of volatile compounds. This superseded the phenolic effect of *T. grandis* after 4 weeks of storage during which *C. gariepinus* could be re-smoked for fresh impartation of the phenol.

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Preservation of fish by exposure to wood smoke is one of the oldest methods. Smoking increases the shelf life of fish as a result of the combined effect of dehydration, antimicrobial and antioxidant activities of several smoke constituents mainly: formaldehyde, carboxylic acids and phenols (Bouriga *et al.*, 2012). Fish and fish products are susceptible to several chemical changes especially during storage as indicated by Total volatile bases in Nitrogen (TVB-N) which is a group of biogenic amines formed in non-fermented food products during storage (Kester and Oyelese, 2018). According to Wu and Bechtel, (2008), TVB-N content of fish is the combined total amount of ammonia (NH3), dimethylamine (DMA) and trimethylamine (TMA) which are products of proteolytic enzymatic reactions on fish protein (Omayma *et al.*, 2013). It is commonly used as an estimate of spoilage of fish (Summers *et al.*, 2016) and has been widely used as an index for freshness of fish. Various indigenous preservatives have been identified with potentials of improving product quality and shelf-life of fish. Information on utilization of these preservatives on African catfish has not been well documented. Therefore, the combined effects of phenol from hardwood (*Tectonia grandis*) and some indigenous preservatives on keeping quality of smoked African catfish were investigated.

MATERIALS AND METHODS

A sample size of 168 *Clarias gariepinus* averaging 550±0.5g was dipped for about one hour in 10.0% salt (FS), 10.0% lime (FLM), 10.0% pepper (FPP), 5.0%

***Email:** christieradeke@gmail.com; tckester@bellsuniversity.edu.ng*

salt and 5.0% lime (FSL), 5.0% salt and 5.0% pepper (FSP), 5.0% lime and 5.0% pepper (FLP), 3.3% salt, 3.3% lime and 3.3% pepper (FSLP) per fish body weight preparations and control 0% preservative (FCL) before smoking between 80 to 100^{0}C for 16 hours using standard traditional smoking kiln and *Tectonia grandis* wood as source of heat. The products were stored for 12 weeks at ambient temperatures (26-28^{0}C). The Phenol contents and Total volatile base-Nitrogen (TVB-N), respectively expressed in meq/kg and mgN/100g were analyzed at 0, 2, 4, 6, 8, 10 and 12 weeks using the methods of Pearson, (1981). Analysis of Variance (ANOVA) was applied to the generated data.

RESULTS AND DISCUSSION

The bi-weekly phenol values in the treated smoked catfish products are shown in Figure 1 to insignificantly differ (P>0.05) among the treatments, respectively ranging between 1.16±0.00 (FS) to 1.31±0.00 mg/kg (FLM). The untreated samples, however, recorded a shorter range of 1.21±0.01 to 1.31±0.00 mg/kg. This implies that though relatively uneven amount of phenol was deposited from the smoking wood (*Tectonia grandis)* onto all the smoked fish products, the impact of the prominent semi-volatile thermal degradation products of wood identified as Methoxyphenols by Hawthorne *et al.* (1989) cited by Albishi *et al.* (2019) was slightly more remarkable on untreated products (FCL) than the treated (FS, FLM, FPP, FSL, FSP, FLP andFSLP). Phenol levels uniquely increased in all the smoked fish samples till week six of storage and dropped gradually thereafter. It can be asserted that the indigenous preservatives affected the volatility of phenol product of wood. The least phenol content of 1.16±0.00 mg/kg recorded in the smoked fish treated with salt (FS) may be explained by the reduction reaction of phenol with sodium to form sodium phenoxide and hydrogen gas as established by Zambrano and Min, (2019). It can apparently be admitted that salt must have slightly hastened phenol volatility. The higher level of 1.31±0.00 mg/kg of phenol recorded in lime-treated fish sample can be indicative of discreet retardation of phenol volatility by the acidity of lime.

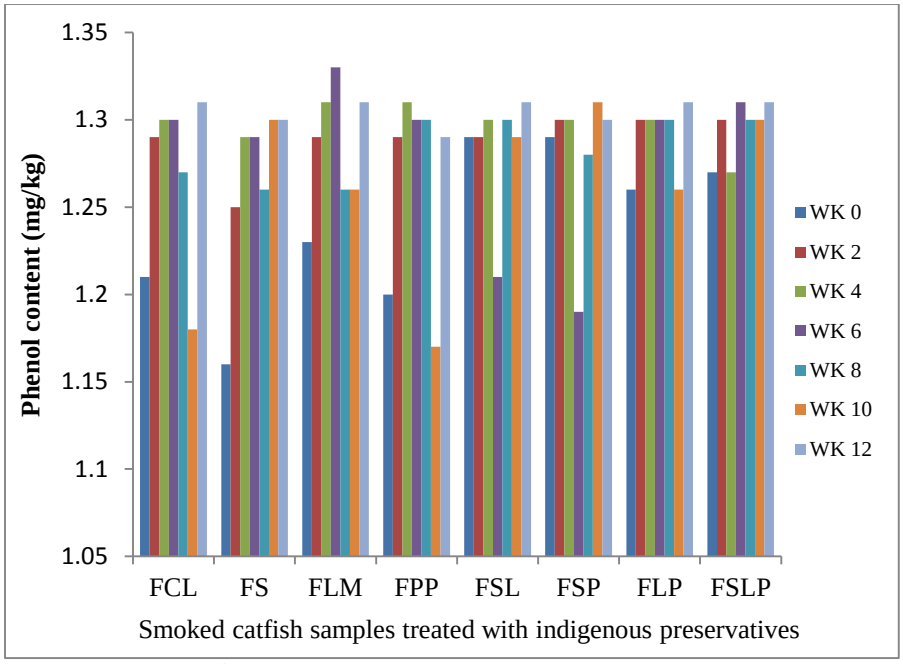

Fig 1. Phenol contents of smoked *Clarias gariepinus* samples pre-treated with indigenous preservatives

Total Volatile Bases in Nitrogen (TVB-N) values differed significantly (p<0.05) among the treatments as shown in Figure 2. Untreated samples ranged from 14.24±0.02 to 31.38±0.03mgN/100g denoting preferred freshness over the treated samples which ranged between 11.06±0.03 (FS) to 128.60±0.04 mgN/100g (FPP). This state of freshness as established by Altissimi *et al*., (2017) that Total volatile base (TVB) nitrogen content of fish is a measure of Ammonia (NH3), dimethylamine (DMA) and trimethylamine (TMA) and commonly used as an estimate of spoilage or index for freshness of fish. The exceptionally highest final value of 128.60±0.04mgN/100g recorded in 10% pepper-treated catfish product superseded the phenolic effect of *T. grandis* and is far beyond the rejection limits of 35–40 mg TVB-N/100 g of fish flesh declared by Connell, (1995) and cited by Idakwo *et al*. (2016).

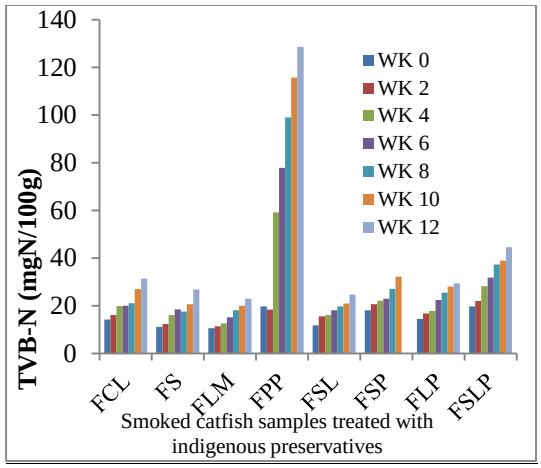

Fig 2 TVB-N values of smoked *Clarias gariepinus* samples pre-treated with indigenous preservatives

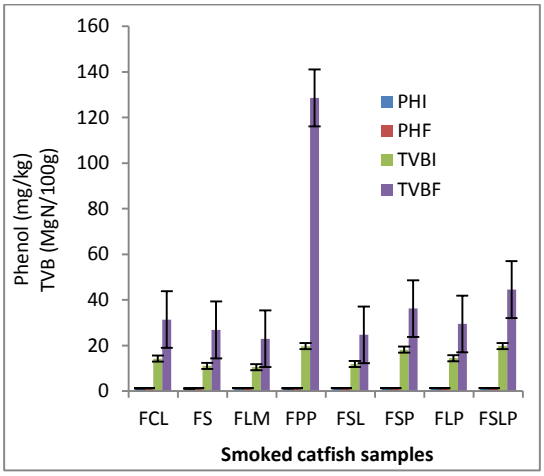

Fig 3: Initial and Final Phenol and TVB-N values of smoked fish samples pre-treated with indigenous preservatives

KEY: *FCL: Fish without preservative, FS: Fish treated with 10.0% Salt, FLM: Fish treated with 10.0% Lime juice, FPP: Fish treated with 10.0% Pepper FSL: Fish treated with 5.0% Salt + 5.0% Lime juice, FSP: Fish treated with 5.0% Salt + 5.0% Pepper, FLP: Fish treated with 5.0% Lime juice + 5.0% Pepper, FSLP: Fish treated with 3.3% Salt + 3.3% Lime juice + 3.3% PepperPHI: Initial Phenol, PHF: Final Phenol, TVBI, Initial TVB, TVBF: Final TVB.*

This obviously shows pepper does not have the ability to inactivate autolytic enzymes and probably spoilage bacteria leading to the formation of high level of volatile compounds, which according to Omayma *et al.* (2013) is related to increase in TVB-N. The comparatively least final TVB-N value of 22.95±0.02mgN/100g was recorded in 10% lime treated products, indicating that lime must have retarded the activities of proteolytic enzymes. This corroborates the finding made by Filiz Uçan *et al.* (2014) in their research findings on effects of different enzymes and concentrations in the production of clarified lemon juice. Figure 3 shows the synergy of the initial and final Phenol and TVB-N values of smoked fish samples pre-treated with indigenous preservatives. Despite the relatively low and insignificantly varied levels of phenol recorded in all the fish samples, the pepper-based treatments; FPP (128.60±0.04), FSP (36.14±0.02), and FSLP (44.53±0.01), could not proffer adequate preservation for 12 weeks, having their TVB-N values exceeding the rejection limits of 35–40 mg TVB-N/100 g of fish flesh (Connell, 1995).

Conclusion: The indigenous preservatives did not have significant effect on the phenol impacted by the *Tectonia grandis* wood on the smoked fish products. Single use of pepper as a preservative should be avoided especially for smoked fish products destined for prolonged storage. Light re-smoking for fresh impartation of the phenol can be done after 4 weeks of storage.

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