

Polycyclic Aromatic Hydrocarbon (PAHs) and Phenols status in some smoked meat products in Nigeria

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Abstract

In under developed and developing country like Nigeria, meat is usually smoked at temperature usually above 400 °C, producing Polycyclic Hydrocarbons (PAHs) and Phenols in meat Products. PAHs compound found in smoked meat exhibit a cancerous substance affecting human health while Phenols in smoked meat are responsible for the smokey aroma and taste. 10 kg of raw meat from semi-membranous muscles of 2 years old male White Fulani cattle was used for this study. The meat was cut into 2 kg each to prepare meat products namely; Kundi, Kilishi, Balangu, Suya and Asun using traditional and oven drying methods. Final samples were evaluated for PAHs, phenols, proximate composition and palatability status. Data were subjected to ANOVA at $P < 0.05$. Results showed that, PAHs had significantly higher values ($P < 0.05$) in Kundi Laboratory smoked, commercially Kundi and Kilishi ($8.00\mu\text{kg}^{-1}$, $8.80\mu\text{kg}^{-1}$, $8.60\mu\text{kg}^{-1}$) respectively while the least was found in Asun ($2.10\mu\text{kg}^{-1}$) for the three samples evaluated. Kilishi had the highest phenols ($P < 0.05$) value ($1.30\mu\text{g}$), while the least was noticed in Asun having ($0.10\mu\text{g}$) in all the three samples evaluated. Kundi products had values significantly ($P < 0.05$) higher in protein and ash content for all samples and the least ($P < 0.05$) in ether extract and moisture content. Balangu and Kilishi had the highest ($P < 0.05$) ether extract while Asun had the highest ($P < 0.05$) moisture content (51.26%, 59.26% and 58.45%) for all the samples evaluated. Balangu, Asun and Kilishi products were rated higher ($P < 0.05$) by the panelists while Kundi products had the least. Irrespective of the processing methods used, the higher the temperature and duration used in smoking, the higher the PAHs and Phenols Compound and the more accumulated the nutrients composition.

Keywords: Kundi, Kilishi, Asun, Balangu, Suya and PAHs.

Introduction

There is high demand for meat in Africa, but unfortunately, meat production falls short of demand. In Nigeria, shortage of meat is not due only to absolute scarcity of animals but often to spoilage as a result of micro-organisms found in meat due to, contamination (Olaoye and Onilude, 2010). Unprocessed meat spoils within hours or days, therefore there is need for value addition (Anna *et al.*, 2005). Adding value to meat involves processing and preservation of meat so as to prolong its shelf-life and improve its acceptability

(Eyas *et al.*, 2006) which includes methods such as canning, pickling, drying and freeze-drying, irradiation, pasteurization, smoking, and addition of chemical additives. Smoking of meat produces several chemical substances such as Formaldehyde, Acetic, Polycyclic Aromatic Hydrocarbon (PAHs) and Phenols etc, from the heat source. Some of these substances cause harm to consumers and endanger a lot of people. PAHs are a group of environmental contaminants that emanate from incomplete combustion of fuel or high temperature pyrolysis of fats and oils (WHO, 2006). It is well known that

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PAHs' occur during curing and smoking of meat and they accumulate on meat products when smoked at high temperature usually above 400 °C over open flames (Viksna *et al.*, 2008). They have been extensively researched into because of their carcinogenicity and mutagenicity to animals and humans (Anyakora, *et al.*, 2008). In 2001, PAHs' ranked 9th on the list of most threatening compounds to human health (King *et al.*, 2002).

The preservation of food (such as meat and fish products) by curing it with wood leads to incomplete combustion, which undoubtedly generate PAHs (Codex 2005). Originally the purpose was to preserve the food, partly by drying and partly by adding anti-microbiological constituents such as phenols from the smoke to the food. At the present time smoking is mainly used to achieve the characteristic taste and appearance of smoked food with preservation playing a minor role. However, smoking has an influence on the shelf life of food because smoke may inhibit growth of some micro-organism depending on the contents of some components like phenols in the smoked food.

Phenols are produced by the prolysis of Lignin which is a highly complex arrangement of interlocked phenolic molecules, they also produce a number of distinctive aromatic elements when burnt, including smoky, spicy, and pungent compounds such as guaiacol, syringol, and sweeter scents such as the vanilla-scented vanillin and clove-like isoeugenol. Guaiacol is the phenolic compound most responsible for the "smokey" taste, while syringol is the primary contributor to smokey aroma (Hui, 2001) and it has been researched into because of its components as far as aromatizing meat products is concerned.

Despite the phenols content (aromatic

thing) in smoked meat, consumption of PAHs in great amount have dangerous effect to the consumers, PAHs is capable of damaging DNA, after they are metabolized by specific enzymes in the body, by a process called bio-activation. Studies have shown that the activity of these enzymes, which can differ among people, may be relevant to cancer risks associated with exposure to this compound (Moonen *et al.*, 2005). Researchers found that high consumption of well done, smoked meat or barbecued meats was found associated with increased risk of colorectal (Cross, 2010) pancreatic (Anderson *et al.*, 2002 and Stolzenberg *et al.*, 2007) and prostate (Cross *et al.*, 2005). In children, the high prenatal exposure to PAHs is associated with lower IQ and childhood asthma (Falco, 2003). And so, out present products need to be check, or work on, so as to minimize the accumulation of PAHs on them.

Therefore, the aim of this study is to evaluate the level of Polycyclic Aromatic Hydrocarbon (PAHs), phenolic status, proximate composition and palatability status in some Nigeria preserved meat products namely; Kilishi, Asun, Suya, Balangu Kundi.

Materials and methods

Source of meat

10kg of raw semi - membranous muscles of 2years old, male While Fulani cattle was used for this study. The muscle was trimmed off of external fat, excess epimysial connective tissues, bone and bone particles, blood vessels and nerves. The meat was cut into 2kg each to produce locally consumed meat products in Nigeria and comparing the laboratory products with the commercially consumed products.

Preparation of Nigeria meat products

Kundi

2 kg of meat from above was used for Kundi production. It was cut in smaller sizes of 10

cm by 12 cm long and 50 -80 g in weight, boiled for 20 minutes at 100 °C and air –dried for 1 hour. The samples were divided into two groups; 1 kg of it was oven – dried at 170 °C, for 2 hours and the other was smoked –dried using coal as heat source at 220 -250 °C for 3 hours. An equivalent product was purchased in the open market as the commercial products.

Kilishi

2 kg of meat was tiny sliced into flat samples of 20 cm by 25 cm and 100 -150 g in weight. Spices were added (groundnut paste called 'labu', monosodium glutamate, and salts) and sundried for 2 hour. 1 kg was oven dried for 3 hours at 170 °C and the other was smoked dried for 2 hours at 220 - 250 °C. An equivalent product was purchased in the open market as the commercial products.

Suya

2 kg of fresh meat was sliced into smaller sizes of 20cm by 25 cm long and 100 – 150 g weight. 1 kg was oven dried for 1 hour at 170 °C and the other 1 kg was smoke dried using coal for 2 hours at 220 – 250 °C, both were then sprayed with suya ingredient containing; onions, grinded dried pepper monosodium glutamate, salt and groundnut oil during processing. An equivalent product was purchased in the open market as the commercial products.

Asun

2 kg of fresh meat was also sliced into 2 groups containing 1 kg each of 10 – 12 cm long and 40– 50 g in weight. One group was oven dried for 45 minutes at 170 °C and the other was smoked dried for 30 minutes at 220 – 250 °C and were both mixed with slight fried pepper stew (fresh pepper of tomatoes and red pepper, monosodium glutamate, curry, thyme and groundnut oil). An equivalent product was purchased in the open market as the commercial products.

Balangu

2 kg of fresh fatty meat areas were cut into small sizes of 10 cm by 12 cm having 40 -50g in weight. 1 kg each was oven dried for 45 minutes at 170 °C and the other was smoked dried at 30 minutes at 220 – 250 °C using coal as the heat source. Both were spray with dried grinded pepper, monosodium glutamate and salt. An equivalent product was purchased in the open market as the commercial products.

Determination of polycyclic aromatic hydrocarbon (PAHs)

1.0g of meat product sample was weighed into a 250 ml beaker; 10ml of carbon tetrachloride was added and stirred with a glass rod to mix properly. The mixture was decanted using a separating funnel into a glass capped 50 ml container. Distilled water was added and shaken vigorously until all materials dissolved. The mixture was allowed to stand out and one quarter (1/4) phase was decanted into a clean 100 ml conical flask. Anhydrous Na₂SO₄ was added to remove all traces of water that may still have been present in the mixture. The resultant clear solution was analyzed on an UV Spectrophotometer using crude oil of working standard range 0-20ppm at a wavelength of 420nm.

% Total Hydrocarbon =

$$\frac{\text{Absorbance of sample extract} \times \text{slope} \times \text{dilution factor}}{10000}$$

Determination of phenol

0.20g of meat product sample was weighed into a 50ml beaker, 20ml of acetone was added and homogenize properly for 1hr to prevent lumping. The mixture was filtered through a Whatman No.1 filter paper into a 100 ml Volumetric Flask using acetone to rinse and made up to mark with distilled water with thorough mixing. 1ml of sample extract was pipette into 50ml Volumetric flask, 20 ml water added, 3 ml of phosphomolybdic acid added followed by

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the addition of 5ml of 23% NaCO₃ and mixed thoroughly, made up to mark with distilled water and allowed to stand for 10min to develop bluish-green colour. Standard Phenol of concentration range 0-10mg/ml was prepared from 100mg/l stock Phenol solution from Sigma-Aldrich chemicals, U.S.A. The absorbance of sample as well as that of standard concentrations of Phenol was read on a Digital Spectrophotometer at a wavelength of 510nm. The percentage Phenol is calculated using the formula:

% Phenol =

$\frac{\text{Absorbance of sample} \times \text{gradient factor} \times \text{dilution factor}}{\text{Wt. of sample} \times 10,000}$

Proximate analysis

Protein, fat, ash and moisture contents of Kilishi, Asun, Suya, Balangu, Kundi/Tinko were analyzed chemically according to the official methods of analysis described by

the Association of Official Analytical Chemist (AOAC, 18TH EDITION, 2000).

Palatability analysis

A total number of twenty trained panelists were selected and they range from ages from 27 – 45 years. The panelists were randomly allocated to the samples. Equal bite from samples was coded and served in an odourless sample on a nine point hedonic scale for tenderness, flavor, colour, juiciness, texture and overall acceptability (Fakolade, 2009).

Statistical analysis and design

The obtained results were subjected to analysis of variance (ANOVA), and significant means were separated using the Duncan's Multiple Range (DMR) test. The SPSS (2007) computer software was used for all statistical analysis using a completely randomized design (CRD).

Results and discussion

Table 1: Polycyclic Aromatic Hydrocarbon (PAHs) μg^{-1} and Phenols (μg) status in meat products

Smoking methods	Meat products	PAHs	Phenol
Lab smoked meat	Kundi	8.00 ^a	0.90 ^b
	Kilisi	6.40 ^b	0.80 ^b
	Balangu	2.50 ^f	0.30 ^c
	Suya	3.20 ^e	0.30 ^c
	Asun	2.10 ^f	0.10 ^d
Lab oven dried meat	Kundi	3.30 ^e	0.40 ^d
	Kilisi	3.30 ^e	0.60 ^c
	Balangu	5.30 ^c	0.20 ^c
	Suya	2.10 ^f	0.20 ^c
	Asun	2.10 ^f	0.10 ^f
Commercial samples	Kundi	8.80 ^a	0.90 ^b
	Kilisi	8.80 ^a	1.30 ^a
	Balangu	8.60 ^a	0.50 ^{cd}
	Suya	4.80 ^d	0.40 ^d
	Asun	2.10 ^f	0.10 ^f
	SEM	0.001	0.001

^{abcdef} means of different alphabet in both the column and row are significantly different (P<0.05).

Lab. Smoked Meat: Laboratory Smoked Meat

Lab. Oven dried Meat: Laboratory Oven dried Meat

Commercially Purchased Samples: Meat products purchased from open market

Table 2: Proximate composition of different meat products (%)

Smoking methods	Meat products	Protein	Ash	Ether Extract	Moisture
Lab smoked meat	Balangu	38.15 ^d	7.05 ^b	12.67 ^a	42.69 ^b
	Suya	51.47 ^c	3.13 ^d	10.10 ^b	35.50 ^c
	Asun	33.25 ^d	6.24 ^c	10.07 ^b	51.26 ^a
	Kundi	78.73 ^a	10.07 ^a	5.24 ^c	7.02 ^e
	Kilishi	63.57 ^b	8.13 ^b	12.20 ^a	14.89 ^d
Lab oven dried meat	Balangu	36.55 ^d	5.06 ^d	10.06 ^b	36.47 ^c
	Suya	47.66 ^c	2.12 ^e	10.17 ^b	43.52 ^b
	Asun	32.10 ^d	5.10 ^d	15.17 ^a	54.26 ^a
	Kundi	77.74 ^a	9.03 ^a	5.02 ^c	7.10 ^e
	Kilishi	60.74 ^b	8.23 ^{ab}	14.01 ^a	16.15 ^d
Commercial samples	Balangu	38.73 ^d	7.04 ^b	14.00 ^a	42.29 ^b
	Suya	48.29 ^c	3.06 ^c	10.01 ^b	38.50 ^c
	Asun	33.43 ^d	7.04 ^b	10.13 ^b	50.45 ^a
	Kundi	79.04 ^a	9.13 ^a	8.09 ^c	6.09 ^d
	Kilishi	65.17 ^b	8.14 ^{ab}	13.17 ^a	13.04 ^d
	SEM	0.01	0.02	0.04	0.00

^{abcd} means of different alphabet in both the column and row are significantly different (P<0.05)

Table 3: Palatability status of different meat products (%)

Smoking methods	Meat products	Colour	Flavour	Tenderness	Juiceness	Texture	Acceptability
Lab smoked meat	Balangu	4.50 ^a	5.00 ^b	6.50 ^a	6.00 ^a	7.25 ^a	7.50 ^a
	Suya	1.75 ^c	5.25 ^{ab}	5.00 ^b	3.25 ^c	3.25 ^c	6.00 ^b
	Asun	2.25 ^b	5.00 ^b	4.00 ^c	4.75 ^b	4.75 ^b	7.25 ^a
	Kundi	1.00 ^d	1.00 ^c	1.25 ^d	1.50 ^d	1.25 ^d	2.00 ^c
	Kilishi	1.75 ^c	5.50 ^a	4.50 ^{cd}	4.50 ^b	4.50 ^b	7.00 ^a
Lab oven dried meat	Balangu	5.50 ^a	4.00 ^b	4.25 ^a	4.00 ^b	4.25 ^a	7.00 ^a
	Suya	1.75 ^c	6.25 ^a	3.50 ^{ab}	3.25 ^c	4.75 ^a	6.80 ^a
	Asun	3.75 ^b	4.00 ^b	4.00 ^b	4.50 ^b	4.75 ^a	5.00 ^b
	Kundi	1.25 ^d	1.50 ^c	1.25 ^c	1.25 ^d	1.50 ^c	2.50 ^c
	Kilishi	1.50 ^c	5.75 ^{ab}	3.00 ^b	5.50 ^a	4.75 ^a	6.60 ^a
	SEM	0.05	0.09	0.08	0.08	0.09	0.07

^{abcd} means of different alphabet along the column are significantly different (p<0.05),

Polycyclic aromatic hydrocarbons (PAHs) are said to be a group of environmental contaminants that emanate from incomplete combustion of fuel or high temperature pyrolysis of fats and oils (WHO, 2006). In Table 1, the PAHs content in all the meat products ranges from (2.10 μkg^{-1} – 8.80 μkg^{-1}). In smoked laboratory and commercial samples of Kundi and Kilishi meat products had the

highest amount of PAHs (6.40 – 8.80 μkg^{-1}) and these values were noticed to exceeds the maximum tolerable limit values set by the Commission Regulation in (2011) for (Bap) Benzo(a)pyrene which is 5.0 μkg^{-1} an indicator for the presence of PAH's. The results obtained were lower than the value (10.5 μkg^{-1}) reported for PAHs in smoked fish samples (Anyakora *et al.*, 2008) and also 10.50 – 66.9 μkg^{-1} reported in Kundi meat

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products (Alonge, 1988). The values observed in this study fell within the values reported by Marta and Mieczyslaw (2007) on PAH's content in four groups of industrial and traditionally produced meat products; ham, cooked cure loins, raw cured loins and medium - ground sausages. When the products were oven dried the values of PAH's on the products were lower than the set limit of 5.0 except for Kilishi with ($5.30 \mu\text{kg}^{-1}$) value and this could be as a result of the heavy groundnut paste used, which could have added oily substances to the surface of the products. This shows that processing meat products using oven dried method could be the best processing method to produce safe meat products for the populace, since it contains lower values of PAHs than the exact lower limit that was recommended and also lower than the smoked and commercial products. It was also observed that the values obtained for Asun, Suya and Balangu were far lower than the maximum limit $5.0 \mu\text{kg}^{-1}$ recommended, which could probably mean that, no matter the type of processing method used, these products will always have low PAHs and as such they are fit for human consumption. Since the time taken to produce Kilishi and Kundi products is lesser, it is advisable to use oven-dried method under controlled temperature, so as to set PAHs in such products under the maximum limit recommended. All processing used in this study were subjected to temperature under 400°C because PAHs concentration becomes high due to pyrolysis of organic matter at high cooking temperatures above 400°C , duration of time used, amounts of fat and oil present and type of cooking (Perez *et al.*, 2004). The presence of high content of PAHs in laboratory smoked Kundi and Kilishi meat products may be as a result of the time used in processing, direct exposure to flame

which lead to more accumulation of PAHs formation and according to data reported in the literature on PAH's on smoked foods are highly variables. (Mottier *et al.*, 2000; Marta and Mieczyslaw, 2007).

Ikeme (1990) reported that about 27 poly – cyclic aromatic hydrocarbons are present in smoked meat, out of these are benz(a)pyrene and dibenz(a,h)anthracene which have been found to be carcinogenic. He also noted that the decomposition of lignin that favour the production of benz(a)pyrene and other poly – cyclic hydrocarbons and production of phenols are greatest at temperature above 400°C . It was then suggested that the best quality smoke is produced at a combustion temperature ranges from $300 - 400^\circ\text{C}$, which could reduces the level of carcinogenic substances. Alonge (1984) also deduced that what is responsible for level of Polycyclic Aromatic Hydrocarbons (PAH's) is not only the lignin or cellulose content of wood but the smoking temperatures. Alonge (1984) describe pyrolysis of wood and that wood consists of approximately 50 % cellulose, 25 % hemicelluloses and 25 % lignin which burn at $200 - 500^\circ\text{C}$. He also describe the 4 stages of pyrolysis of wood; stage 1, at temperature up to 170°C , thorough drying of wood take place, stage 2; at $200 - 260^\circ\text{C}$, pyrolysis of hemicelluloses, at the junction, a light brown condensate which contains pentasanes, alpha cellulose carbonase and acetic acid is formed. Stage 3; at $260 - 310^\circ\text{C}$, pyrolysis of cellulose, cellulose is broken down forming Co_2 , acetic acid and formal acids. Stages 4; at $310 - 500^\circ\text{C}$, pyrolysis of lignin becomes exothermic forming a reddish brown condensate containing large number of compound. At stage 4, PAHs is often produced, that is why smoking or processing below 400°C as reported by Ikeme (1990) could help to reduced PAHs in meat smoked or processed.

Table 1 also shows the phenol compound present in all the meat products and they fell between (0.10µg – 1.30 µg) having the highest level phenol compound in Kilishi for commercially purchased samples and this could be as a result of the spices used and the way it was prepared. The levels of phenols were significantly lower in Asun in the three samples evaluated, and this could be due to the method of preparation of Asun which requires a shorter duration for the processing. It was also observed that the values obtained for oven dried methods of all the meat products are low in phenols which could mean that phenols could mostly be found in wood, since coal was used as the heat source. Wikipedia (2002), noticed that about 20 phenols have been isolated from wood smoke and identified. Alonge (1984) also reported that about 45 phenolic compounds are present in wood smoke and they are formed by pyrolysis of lignin which degrades to ferulacid and sinapinard which are further decomposed to produce the main components of phenols; guaiacol and syringol. Toth *et al.* (1984) said soft wood produces guaiacol and its analogous substitutes while syringol and its derivatives appear mainly in the smoke of hard woods. Hamm and Pothast (1976) discovered that the total phenol contents of smoke rises from 380 - 600 °C and drops again as the temperature increases above 700 °C. In this study, the temperature used for all the products produced are less than 300 °C leading to a very low amount of phenols in the products, except for commercially produced Kilishi. Phenols are very important in meat products since it act as antioxidants, contribute to meat colour, add smoky taste, have bacteristatic effect and contribute to the flavor of the products.

Table 3, shows the proximate composition of meat products produced. Kundi had the

highest ($P<0.05$) protein content (77.04 – 78.73%) than other samples evaluated while Asun had the least value. The highest protein in kundi products corresponds with the report by Soniran and Okubanjo (2002) for protein content of pork loin (69.8– 79.1%). Kumar and Alsberg (2008) who reported protein content for sun dried and oven dried Kundi ranges from (68.1 – 71.8%). The results gotten could be due to the conformational changes of protein on heating which is known as denaturation, followed by structural changes which occur during heating which are referred to protein-protein interactions, resulting in the aggregation of proteins (Tornberg, 2005). Also, the duration used in producing these and the temperature used had effect on the accumulation of their nutrients. Kundi and Kilishi spent longer time than the other products. The time spent and temperature used could be describe accordingly; Kundi → Kilishi → Suya → Balangu → Asun. Ash content is an indicator of the mineral content of meat or the mineral profile was observed to follow the same trend as the protein content and this could also be due to longer time of drying process and the temperature degree used and the accumulation of mineral from the coal which could have stick to the surface of the meat. The ash content obtained fell within the range of 10.6, 15.2 and 7.4 % for cure ham, meat vegetables extract and jerked beef, reported by (Fernandez – Salguero *et al.*, 1993).

Ether Extract content were observed highest in Balangu and Kilishi products (12.67 – 15.17) and (12.20 – 14.01) respectively. This increase could result from the meat and method used in processing, while the least values are observed in Kundi products (5.02 – 6.01%). The meat used for balangu is fatty, while during Kilishi processing, vegetable oil are often sprinkle. The values obtained in

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this study are lower than the values (10.9 - 29.6) reported by Vania (2006) for fat content of alheria meat. Asun had the highest ($P < 0.05$) value of 20.45 - 54.26 % for moisture content while the least value was observed in Kundi with 6.09 - 7.10 %. The values obtained are in line with (40.17 - 57.17%) reported by Edema *et al.* (2008) for moisture content of smoked meat products. Hedrick *et al.* (1994) reported an inverse relationship between moisture and fat content of the meat. However in this study, the products with more ether extract were noticed to have more moisture content.

Table 4, shows the palatability characteristics of meat product used. The results obtained showed that Balangu, Kilishi and Asun had the highest value for overall acceptability in both the laboratory smoked and oven dried processing method. The panelists rated both processing for Balangu products higher ($P < 0.05$), since Balangu had the highest ether extract content in the proximate composition and fat modifies the perception of flavor compounds by influencing, release of flavours and by affecting their distribution and migration (Das *et al.*, 2009). Kilishi is also high in flavour and its acceptability are (5.63 and 6.50%) which could be due to the value added e.g, groundnut paste and spices. It was observed that for the three product rated, the flavor, texture and juiciness were rated higher by the panelist than the rest products, which had a strong effect on the overall acceptability. Lowest level for acceptability was obtained in Kundi meat in all the palatability status and this could be due to it texture (very dry) having 1.25 and 1.50 values and low perceptible of the products because Kundi unlike other products need no spices, ingredient or salt to improve the flavor or taste of the products. In Nigeria, Kundi is a

ready-to-cook meat products while others produced are ready-to-eat products. The process used in this production reduces the moisture content which in turn affects the juiciness of the meat, thereby affecting the overall acceptability, since overall acceptability depends on Juiciness, texture and flavor of meat products. (Fakolade, 2011).

Conclusion

Kundi and Kilishi had the highest percentage nutrients, phenols and PAHs for smoked dried and commercial produced products. The Oven dried samples are safe for consumption, having values less than the maximum recommended limit $5.0 \mu\text{kg}^{-1}$ set by the Commission Regulation (2011). Balangu, Kilishi and Asun were rated highest having the highest flavor, texture, juiciness and higher ether extract.

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