

Physicochemical Properties and Fatty Acid Profile of Bean Cake and Buns Oil Extract

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ABSTRACT

Background and Objective: Vegetable oils are obtained from plant sources and are mainly used in cooking. In the process of cooking, the oil is incorporated into the final fried food product. There has been a substantial increase in the consumption of fried foods. In this research, the physicochemical properties and fatty acid profile of vegetable oil contained in popularly consumed fried foods (Bean cakes and Buns) were analyzed to ascertain its suitability for consumption when compared to pure vegetable oil.

Materials and Methods: The 800 g of samples of Bean cakes and Buns were purchased at random; the samples were air dried and the oil was extracted from the samples by cold extraction method. The extracted oils were subjected to analysis; the physicochemical properties determination was carried out using the methods of AOAC and the fatty acid profile was determined using the gas chromatographic method. The results obtained were subjected to statistical analysis using the t-test.

Results: The physicochemical properties of the oils reviewed were found to be at the range concentrations as follows: Saponification value: 251-537 mg/kg, iodine value: 39.37-83.44 g I₂/100 g, peroxide value: 18-21.82 mEq/kg, acid value: 0.847-20.40%, specific gravity: 0.834-0.865, viscosity: 47-68 mPa/S, water content: 1.491-1.899%, boiling point: 72-122°C, freezing point: 9-11°C, melting point: 18-30°C and smoke point: 194-256°C. The fatty acid profile revealed that the oils from the fried foods contained less unsaturated fatty acids than the pure vegetable oil. **Conclusion:** The study showed that Bean cakes and Buns should be consumed in moderation as they can hurt the overall health of an individual.

KEYWORDS

Bean cake, fatty acid profile, physicochemical property, buns, vegetable oil

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INTRODUCTION

Vegetable oils are oils made from the seeds of plants. They enhance the flavor and color of food and are a good source of lipids and fatty acids. Vegetable oils provide the two essential fatty acids that the human body is unable to synthesize¹. Vegetable oils supply energy and required fatty acids². In the industrial sector, they are crucial to the development of various chemical products, medications, paints, cosmetics and above all food³.

Vegetable oils are mostly used for cooking and frying foods and snacks whereby the food is immersed in hot oil at high temperature⁴. The high temperature has been recognized as one of the factors that alter the quality of oil⁵. The quality of oils is very important and the extent of the oil quality can determine its desirable use. The feature of any oil is indicated by numerous physical and chemical properties which indicate both the nutritive and physical quality of the oil⁶. The properties include saponification value, iodine value, peroxide value, viscosity, water content, acid value, specific gravity, freezing point, melting point, boiling point, smoke point⁷, etc. The specific value of some of these properties is used to determine the shelf-life quality of oils⁸.

Vegetable oils are made up of over 90% glycerin esters and fatty acids, which are distinguished by the structure of the triglycerol and the proportion of saturated and unsaturated fatty acids. The cis fatty acids are converted into trans fatty acids during the partial hydrogenation of fats and oils, these trans fatty acids formed are capable of affecting the human serum lipoproteins and the risk of coronary heart disease⁶. Vegetable oils containing fatty acids in cis configuration are nutritionally significant. The quantity and quality of the fatty acids consumed in the diet play a critical role in the health and disease of the individual. Fried foods have desirable flavor, color and crispy texture which makes them very popular among consumers⁸. Bean cake (Akara) is a deep-fat fried ball product that is made from Cowpea (black-eyed peas) flavored with salt, fresh onions and pepper by street and market vendors as well as in the home. It is widely consumed in Nigeria and West Africa at large, as a cheap source of protein. It is abundant in calories, fiber, minerals, vitamins, antioxidants and fats.

Buns, a deep-fried food in the form of soft bread rolls, are typically made from flour, yeast, sugar and water and are consumed as a dietary staple by a significant portion of the population. They contain certain nutritional elements such as carbohydrates, fats, vitamins and minerals whose quantity is dependent on several factors such as variations in ingredients, cooking methods, cultural variations, portion size, etc. This study aimed at analyzing and comparing the physicochemical properties and fatty acid profile of oil extracted from deep-fried foods (Buns and Bean cake) to pure vegetable oil obtained from commercial vendors in Ifite-Awka, Anambra State, to ascertain the suitability for consumption.

MATERIALS AND METHODS

Study area: The study was carried out at the Department of Biochemistry Research Laboratory, Faculty of Natural and Applied Sciences, Nnamdi Azikiwe University, Awka, Nigeria, from April to May, 2023. The Biochemistry Laboratory conducted the preparation of the sample and oil extraction, while Docchy Analytical Laboratories and Environment Services Limited, Awka, Nigeria conducted the physicochemical property and fatty acid composition analysis of the oil samples.

Sample collection and preparation: Freshly fried buns (800 g) and Bean cakes (800 g) were purchased from commercial vendors in Ifite-Awka, Anambra. The buns and Bean cake were taken to the laboratory, where they were cut into pieces, weighed and oven (Microsil, India), and dried at 60°C for 24 hrs, after which they were ground into powdered form to be used for the analysis of the physicochemical properties and fatty acid profile.

Oil extraction from the samples (cold extraction): The ground samples (Buns and Bean cake) were poured into air-tight jars with an unspecified amount of n-hexane added, just enough to extract the oil from the samples. The mixtures were left to stand for 3 hrs, after which they were filtered using filter paper. The crude extracts obtained were transferred into beakers and placed in the oven at 75°C to extract the oil. The n-hexane and other components contained in the crude extracts evaporated during this process, with the extracted oil left in the beakers.

Determination of physicochemical properties: The physicochemical properties determination of the extracted oil from Buns and Bean cake and pure vegetable oil was carried out using the methods of AOAC and Helrich⁹. The physicochemical properties include saponification value, iodine value, peroxide value, acid value, specific gravity, viscosity, water content, boiling point, freezing point, melting point and smoke point.

Saponification value: It is a measure of the amount of alkali required to completely saponify a certain quantity of oil. It is a measure of all the saponifiable fatty acids (including the esters) present in oil. The 2 g of oil was weighed into a conical flask and 25 mL of 12% alcoholic potassium hydroxide solution was added. A reflux condenser was attached to the flask and it was heated for 1 hr. Five drops of phenolphthalein indicator were then added and the solution was titrated with 0.5 M hydrochloric acid (Titration = a mL).

A blank was prepared at the same time (Titration = b mL).

Calculation⁹:

$$\text{Saponification} = \frac{(b - a) \times 28.05}{\text{Weight of sample (g)}}$$

where, a represents sample titer with (Titration = a mL) and b represents blank titer (Titration = b mL).

Iodine value: The iodine value is a simple constant used to measure the degree of unsaturation or the average number of double bonds in an oil sample. It is the number of grams of iodine that could be used to halogenate 100 g of oil. As 0.3 g of oil was weighed out into a conical flask. A 10 mL of carbon tetrachloride was added to the oil. Twenty milliliters of Wij's solution was added. The flask was then covered with foil and allowed to stand in the dark for 30 min. Fifteen milliliters of 10% potassium iodide was added, followed by 100 mL of water. It was mixed and titrated with 0.1 M sodium thiosulphate solution using starch as an indicator (Titration = a mL).

A blank was also prepared (Titration = b mL).

Calculation⁹:

$$\text{Iodine value} = \frac{(b - a) \times 1.269}{\text{Weight of sample (g)}}$$

where a represents sample titer with (Titration = a mL) and b represents blank titer (Titration = b mL).

Preparation of Wij's solution: Eight grams of iodine trichloride was dissolved in 200 mL of glacial acetic acid. Nine grams of iodine crystals were dissolved in 300 mL of carbon tetrachloride. The two solutions were mixed and diluted to 1000 mL with glacial acetic acid.

Peroxide value: It indicates the degree of oxidation or rancidity in the oil sample. It is a measure of the number of peroxides present in oil. A higher peroxide value suggests a higher level of oxidation which can affect the quality and taste of the oil. One gram of oil was weighed out into a boiling tube and 1 g of potassium iodide was added. Twenty milliliters of a solvent mixture containing glacial acetic acid and isopropyl in a ratio of 2:1 was added. It was then boiled for 30 sec at 40°C and subsequently for 30 sec at 100°C. The content was poured into a flask containing 20 mL of 5% potassium iodide and titrated with 0.002 M sodium thiosulphate solution using 1 mL of starch as an indicator (Titration = a mL). Blank was prepared at the same time (Titration = b mL).

Acid value: The acid value determines the amount of free fatty acids present in an oil sample. A low acid value indicates that the sample contains less free fatty acids, thus reducing its exposure to rancidity, vice versa.

A solvent mixture of 10 mL of petroleum ether and 10 mL of ethanol was prepared. Five drops of phenolphthalein were added to the solvent mixture. Two grams of oil was dissolved in the mixed neutral solvent. It was then titrated with 0.1 M hydrochloric acid (Titration = a mL). Blank was also prepared (Titration = b mL).

Calculation⁹:

$$\text{Acid value} = \frac{\text{Titer value} \times 5.61}{\text{Weight of sample (g)}}$$

Specific gravity: It refers to the density of an oil sample compared to the density of water. It helps determine the buoyancy and relative weight of oil.

A 50 mL pycnometer (PYC 100 OHAUS, USA) was washed with detergent water and petroleum ether and dried. It was then filled with water, weighed and dried. After it was dried, it was filled with an oil sample and weighed.

Calculation⁹:

$$\text{Specific gravity} = \frac{\text{Weight of sample (g)}}{\text{Weight of water (mL)}}$$

Viscosity: It refers to the thickness or flow resistance of the oil. It measures how easily the oil can flow. High viscosity indicates thickness and slow flow and vice versa.

The oil was poured into a bottle and set to the viscometer (Foshan Yali, China). Using a rotational viscometer, the viscosity of the oil was measured.

Water content: It is the measure of the moisture or water concentration within the oil. It can indicate the level of water impurities or contamination in the oil. The weight of a crucible was taken. Two grams of oil was weighed into the crucible. It was placed in the oven for 3 hrs, after which it was allowed to cool and weighed (weight of crucible and oil after drying).

Boiling point: It is the temperature at which it changes from a liquid to gas. Different oils have different boiling points depending on their chemical composition.

Ten milliliters of oil was measured. It was heated at a constant temperature of 100°C. A thermometer (Finlab, Enugu State, Nigeria) was dipped into it to determine its temperature as soon as it started boiling.

Freezing point: It is the temperature at which the oil sample changes from liquid to solid when cooled. Ten milliliters of oil was measured and placed in a freezer (LG Electronics Inc, Seoul, Korea). The temperature at which it forms crystals was read.

Melting point: The melting point is the temperature at which the oil changes from a solid to a liquid state. A thermometer was inserted into the previously frozen oil the moment it melted. The temperature was read.

Smoke point: It is the temperature at which the oil starts to produce smoke and breaks down when heated. Different oils have different smoke points, which can vary depending on factors such as their composition and purity. Ten milliliters of oil was measured and heated. A thermometer was inserted to read its temperature as soon as it started releasing smoke.

Determination of fatty acid profile: This was determined using the gas chromatographic method (Agilent7890 Technologies, USA).

The sample was prepared by using the following protocol: Three milliliters of oil was measured into a separating funnel and was dissolved with 2 mL of chloroform. Methanol was added in an unspecified amount. The chloroform and methanol dissolve and extract the analyte from the oil. Upon the addition of methanol, three layers were formed. The chloroform layer which was at the bottom of the separating funnel was carefully transferred into a small tube for injection.

Fixed setting: The flame was ignited with helium as the carrier gas at a flow of 0.8 mL/min. The gas chromatograph is equipped with an on-column, auto-injector, detector, SP-2560 capillary column (100 m×0.25 mm). Pressure, flow and velocity of the column were set to 13.8 psi, 0.8 mL/min and 21 cm/sec, respectively. The temperature of the detector and injector was set to 250°C. The temperature and pressure of the front inlet were also set to 300 and 13.8 psi, respectively. The sample tubes were placed into the auto-injector and the oven's initial temperature of 60°C was held for 1 min, it was then ramped at 15°C/min to 165°C and held for 1 min and finally ramped at 2°C/min to 225°C. The GC was allowed to warm up. When the instrument was ready, the "NOT READY" light turned off and the "RUN" began. The analysis lasted 45 min.

RESULTS AND DISCUSSION

From Table 1, vegetable oil showed the highest levels of smoke point (256°C), freezing point (11°C), boiling point (122°C) and acid value (14.129%) while the oil from Bean cake and Buns showed higher levels of saponification value (516 and 537 mg/kg), peroxide value (21.82 and 20.85 mEq/kg), water content (1.810 and 1.899%) and melting point (30 and 22°C) respectively. Buns showed the lowest levels of iodine value (39.37 gI₂/100 g) and viscosity (47 mPa/S). The three oil samples were similar in the values of their specific gravity.

From the result of the fatty acid profile (Table 2), saturated fatty acids (myristic and palmitic acid) were found to be significantly higher in pure vegetable oil (113.76 and 232.58 mg KOH/g) than in Bean cake (1.09 and 5.74 mg KOH/g) and Buns (1.88 and 5.75 mg KOH/g). Lauric acid, a saturated fatty acid was found in Bean cake and Buns but not in vegetable oil.

Unsaturated fatty acids (oleic, linoleic and linolenic acids) were found in the samples but significantly higher in pure vegetable oil (2363.49, 159.67 and 1760.23 mg KOH/g) than in Bean cake (22.92, 31.32 and 61.76 mg KOH/g) and Buns (42.75, 2.37 and 100.03 mg KOH/g). Docosahexaenoic acid was found in Bean cake and Buns but absent in pure vegetable oil.

Table 1: Physicochemical properties of oil extracted from Bean cake and Buns compared to pure vegetable oil

Physicochemical parameter	Beancake (Akara)	Buns	Vegetable oil
Saponification value (mg/kg)	516.00	537.00	251.80
Iodine value (g _{I₂} /100 g)	83.44	39.37	80.52
Peroxide value (mEq/kg)	21.82	20.85	18.00
Acid value (%)	20.400	14.129	0.847
Specific gravity	0.865	0.845	0.834
Viscosity (mPa/S)	47	68	52
Water content (%)	1.810	1.899	1.491
Boiling point (°C)	98	72	122
Freezing point (°C)	9	10	11
Melting point (°C)	22	30	18
Smoke point (°C)	194	204	256

Table 2: Fatty acid profile of oil from Bean cake and Buns vs pure vegetable oil

Component	Name	Bean cake (Akara) (mg KOH/g)	Buns (mg KOH/g)	Vegetable oil (mg KOH/g)
C12	Lauric acid	13.04	12.08	-
C14	Myristic acid	1.09	1.88	113.76
C16	Palmitic acid	5.74	5.75	232.58
C18:1	Oleic acid	22.92	42.75	2363.49
C18:2	Linoleic acid	31.32	2.37	159.67
C18:3	Linolenic acid	61.76	100.03	1760.23
C22:6	Docosaheptaenoic acid	39.59	64.39	

Lipids and triacylglycerol occur in oils. The chemical composition includes saturated and unsaturated fatty acids and glycerides. Vegetable oils are constituents of daily diet, which provide energy and essential fatty acids and serve as a carrier of fat-soluble vitamins.

Deep frying and repeated deep frying can cause several oxidative and thermal reactions which can lead to changes in the physicochemical, nutritional and sensory properties of the oil and fried food¹⁰. During frying, the hydrolysis, oxidation and polymerization processes change the composition of oil, the flavor and the stability of its compounds¹¹. Again, reaction with oxygen can cause structural degradation in the oil which leads to loss of quality of food and is harmful to human health¹².

The temperature has been recognized as one of the factors that reduce oil quality⁵. Elevated temperature is a factor that causes the increased acid value in oils¹³. The high acid value indicates high free fatty acid, which causes oil to become rancid. It has been demonstrated that elevated free fatty acids, change of color, low smoke point, low iodine values, elevated total polar materials, high peroxide values, high foaming properties and increased viscosity are indicators of poor oil quality¹⁴. Pan *et al.*¹⁵ and He *et al.*¹⁶ studied the impact of temperature on the stability, viscosity, peroxide value and iodine value to assess the quality and functionality of the oil.

Recently, the effect of heating oil and prolonged heating time on the physicochemical properties of cooking oil was investigated by Nduka *et al.*⁴. The results showed that there were significant differences in the physicochemical properties of the oils. Omara *et al.*¹⁷ investigated the effect of continuous deep-fat frying on the physicochemical properties of oils. Their results showed that changes in the physical and chemical parameters increase with the increase in the number of fries. In another study, Ilyas¹⁸ examined the physicochemical properties of oils and the results revealed that acid value and specific gravity and iodine values are below the safety limit.

Oils are mixtures of triglycerides (TGs) and their viscosity depends on the nature of the TGs present in the oil. The viscosity changed due to the different arrangement of the fatty acids on the glycerol backbone of the triglyceride molecule. Therefore, viscosity is related to the chemical properties of the oils such as chain length and saturation or unsaturation. The viscosity value is high above the reference value that was 33 mPas reported by Fasina and Colley¹⁹. Table 1 shows that the viscosity is high in buns oil as compared to bean cake oil and vegetable oil has a high boiling point relative to buns oil. Results showed that oil

viscosity was above the reference value of 35 mPas²⁰. Oil's viscosity was above the value of 40 mPas²¹. Viscosity also depends on temperature. When temperature increases kinetic energy also increases that has improved the motion of molecules and reduces intermolecular forces. The layers of the liquid pass easily over each other and thereby contribute to reducing the viscosity²². Such a phenomenon is confirmed by other researchers since the increase in viscosity may be probable due to high saturation of the triglyceride chain whereas the decrease is likely due to an increase in unsaturation²³. This explains that the viscosity and density decrease with an increase in unsaturation and increase with high saturation and polymerization²³.

During frying thermo-oxidative, lipid oxidation and hydrolytic reactions take place resulting in deterioration in the quality of the frying oil and food²⁴. The primary oxidation products, the hydroperoxides, may break down to lower molecular weight compounds, such as free fatty acids, alcohols, aldehydes and ketones, eventually leading to a rancid product. Lipid oxidation is a deteriorative process with implications for the quality and value of the oils, especially in relation to the off-flavors as a result of autoxidation²⁵. The presence of air and water accelerated the deterioration of frying oil) and increased the number of polar molecules.

The iodine value (IV) measures the degree of unsaturation in vegetable oil. It determines the stability of oils to oxidation and allows the overall unsaturation, to be determined qualitatively²⁶. It was observed that measured iodine values for beancake, buns and vegetable oils are 83.44, 39.37 and 80.52 g, respectively. The iodine values obtained for the oil samples indicated that the iodine value of oil is below the Codex standard recommended range (124-139 mg/100 g)²⁷. The result is significant with the providing range of 48-58 mg/100 g²⁸. The iodine value decreased when heated, due to breakage and saturation of bonds. These low iodine values may have contributed to its greater oxidative storage stability. The oxidative and chemical changes in oils during storage are characterized by increased levels of free fatty acid and reduction in the total unsaturation of oils²².

Saponification value (SV) is an index of the average molecular mass of fatty acid in the oil sample and it is used in checking adulteration of the oil samples²². The SV value obtained for the oil samples in Table 1 showed a saponification value of above 500 mg KOH/g for Bean cake and Bun oil extract. The values are above the expected range of 195–205 mg KOH/g of oil as specified by the Standard Organization of Nigeria (SON)²⁹ and Nigerian Industrial Standards (NIS)³⁰. The higher value of saponification values suggests that the mean molecular weight of fatty acids is high or that the number of ester bonds is greater. This might imply that the fat molecules did not interact with each other.

Acid value (AV) represents the mg KOH required to neutralize the free fatty acid in 1 g of oil while free fatty acid (FFA) is the percentage by weight of a specified fatty acid such as percent oleic acid in oil. Therefore, the acid value is a good indicator of soil degradation caused by hydrolysis or enzymes³¹. In this present study, as seen in Table 1, bean cake oil had the highest acid value (20.400 mg KOH/g) among the other sample oils. A higher acid value implies a lower quality of oil and the oil is going to be rancid³². The distinction of acid value in our trials could be due to variance in moisture contents.

Peroxide value (PV) is a useful indicator to measure the rancidity level of fats and oils and also it could be used as an indication of the quality and stability of fats and oils³³. It measures the extent to which rancidity reactions have occurred during storage³³. The peroxide value was also found to increase with the storage time, temperature and contact with the air of the oil samples. The PV values in Table 1 for all the oils range from 18-21.82 meq/kg. The peroxide value determines the extent to which the oil has undergone rancidity. Peroxide value ranges are highly related to the standard value of 10 meq/kg specified by Udensi and Iroegbu²⁹ and Wazed *et al.*³⁰. Fresh oils have peroxide values lower than 10 meq O₂/kg and before oil becomes rancid, its peroxide value is between 20 and 40 meq O₂/kg³⁴. The peroxide value was also found to increase with the temperature and contact with the air of the oil samples²².

Of all the oils, only bean cake oil showed the highest peroxide value while vegetable oil showed a lower peroxide value. The lower value of peroxide implied that oil is less susceptible to rancidity. Besides, the fluctuation in the peroxide values of oil can be attributed to the decomposition of the peroxides that are formed during primary oxidation to secondary oxidation.

The smoke point indicates the breakdown of fats to glycerol³⁵. As shown in Table 1, the smoke point of all samples was higher than the standard limit (170°C). It was shown that smoke point is dependent on FFA content and refinement process. Essien *et al.*³⁶ reported the smoke point of 184.86°C for sesame oil³⁶ which is lower than current results. In general, the high smoke point oils have better thermal stability during frying³⁷.

The presence of oil in the human diet is important due to providing energy, nutrients and vitamins. The predominant fatty acids in all oil samples were estimated as linoleic acid, oleic acid and palmitic acid, which was consistent with the results of Ghosh *et al.*³⁸ and Naz *et al.*³⁹. The presence of high oleic acid and total monounsaturated fatty acids in oils might have a protective role in cardiovascular diseases⁴⁰. However, the minor components, positional distribution of the glycerol backbone of fatty acids and type of antioxidants could be considered important for oil susceptibility to oxidation⁴¹. It was mentioned that differences in the composition of oleic and linoleic fatty acids could cause some changes in oil composition. Oil samples with linoleic fatty acids higher than 50% are considered polyunsaturated oils⁴¹. In the current study, linoleic fatty acids of vegetable oil samples with 54.55% were determined higher than other oils. All these physicochemical parameters such as viscosity, peroxide value, iodine value and saponification values are properties of oils.

Deep frying and the use of the same oil for frying many times is a general practice mostly in commercial and sometimes in domestic cooking processes. This practice generates lipid peroxidation products that may be harmful to human health. Most of these compounds are non-volatile and they remain in the frying oil; affecting its physical properties and causing the oxidative degradation and the partial conversion of lipids to volatile chain-scission products, non-volatile oxidized derivatives and dimeric, polymeric or cyclic substances leading to the formation of toxic and carcinogenic compounds.

CONCLUSION

The physicochemical analysis and fatty acid profile of oils carried out showed that the consumption of these fried foods (Bean cake and Buns) should be in moderation as the oil contained in them can be detrimental to health. Also, the duration of heating of oil can be reduced and vegetable oil with a high smoke point should be used to minimize the negative cascade of changes that occurs. It is recommended that advanced studies should be accomplished to appraise the nutritional value, heavy metals profile and antimicrobial activities of oils in deep fry local snacks.

SIGNIFICANCE STATEMENT

Akara (Bean cake) and Buns are deep oil-fried local snacks, consumed in Nigeria. In Nigeria, the oils used for the production of these local snacks are often reused in repeated frying and the oil is replenishment with fresh oil, as the quantity reduces. The purpose of this study is to analyze the oil extracted from "Akara" and "Buns"; the objective is to compare the physicochemical properties and fatty acid profile of the oil extracted to pure vegetable oil. The result implied that some reactions occur during frying that have consequences on the properties of the snacks. Exposures to heat enhance the oil deterioration and continuous use of such oils could be harmful to health. It is essential to monitor the quality of oil to avoid the use of degraded oil and the quality of residual oil in the snacks to ascertain their suitability for consumption.

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