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Comparative Proximate Analysis of Rice Husk Oil and Commercially Available Vegetable Oil

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Abstract

Rice husk is a by-product of rice milling and it is used as a valued raw material for different purposes. Rice husk oil was extracted and analysed for minerals such as calcium, magnesium, phosphorus, iron, potassium and sodium using Atomic Absorption Spectroscopy (AAS). Commercialized vegetable oil sourced from the market was also analysed for the same set of minerals and the results were compared. The comparison showed that rice husk oil is better for consumption than vegetable oil because of its high concentration of calcium, magnesium and phosphorus. Proximate analysis of the rice husk was also determined and the result showed that rice husk has 19.000% Ash, 14.300% Carbohydrate, 45.500% Crude fibre, 4.800% Fat, 8.600% Moisture and 7.800% Protein. The result of silica content determination also shows that rice husk ash contains 92.000% silica.

Keywords: Rice bran, biomass, proximate analysis, characterization, silica

1. Introduction

Energy has been recognized as been essential for social development, economic growth and as well as life quality (Hazar, 2010). Due to increase in urbanization and industrialization energy demands worldwide have increased tremendously (Hazar, 2010). Biomass is known as a clean and renewable source of energy. The conversion of biomass into other various usages is getting increasing attention (Chen *et al.*, 2010) and is a good and promising source for the production of various energy-related products. These products include liquid, solid, gaseous fuel, heat, chemical electricity and other materials. One of the potentials ways for the alternative utilization of biomass is thermo-chemical conversion (Karagoz *et al.*, 2005).

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Recently hydrothermal process became an important procedure in the chemical conversion of biomass with its environmental friendliness being one of its major advantages. The process at low temperature (Karagoz *et al.*, 2004), under the use of the thermochemical process liquefaction (Agudo *et al.*, 2000), gasification (Watanbe *et al.*, 2003) and combustion have been widely studied (Gayan *et al.*, 2004). Nigeria with a population estimated to be 184.7 million as at September, 2015 (www.worldometers.info), mostly depends on palm oil, groundnut oil and soybeans oil as edible oil. With a vast increase in population there is the need to look for alternative edible oils other than the ones listed above. Rice is regarded as a very important staple food for nearly half of the world's population (Slayton and Timmer, 2008). More than seventy countries, mostly, Asian countries, produce and consume rice.

African countries like Nigeria are not left behind in the production of rice. An example is the Igbemo rice (brown rice) which is grown and milled in Southwest Nigeria. Most Nigeria prefer the consumption of local rice because of the pleasant taste and smell (Longton, 2000). Rice husk is one of the world's most widely available agricultural wastes (Giddel and Jivan, 2007; Suyidani and Muryanto, 2012). Worldwide, approximately 600 million tons of rice paddy is produced each year. An annual total production of 120 million tones is produced and an average of 20% of the rice paddy is husk (Giddel and Jivan, 2007). Rice husk (or rice hulls) is the hard protecting skin that covers the grain and is removed from rice seed as a by-product during mill processing (Sudiyan and Muryanto, 2012). In many of the rice producing countries, most of the products from rice processing is either dumped as waste or burnt (Kumar *et al.*, 2012). Rice husk is thus a major environmental problem because of its low commercial value (Kumar *et al.*, 2012). Heavy metals especially have been known as one of the major environmental pollutants as discussed by Okoro and Co-workers in their previous research on environmental studies (Okoro *et al.*, 2016a; Okoro *et al.*, 2016b; Okoro *et al.*, 2017).

Rice oil can be obtained by extraction or milling of the rice husk, while the resultant rice bran can be used as animal feed. Stabilized rice bran is used in food industry as a source of dietary fibre, protein and desirable oil but less than ten per cent of this valuable oil is used for edible oil production. Waste rice bran can as well be used as bio-adsorbents in reducing toxic metals in the environment (Mathew *et al.*, 2016). Due to the nutritional benefits of rice bran oil and rice husk, this research focuses on characterization of the rice bran oil, proximate analysis and determination of the essential metals in the rice husk. In addition, evaluation of the feasibility

of replacing n-hexane with methanol for the extraction of the oil from rice bran and extraction time for both solvents used was investigated (N-Hexane and methanol).

2. Materials and Methods

Sample Collection and Sample Preparation

Rice husk was obtained from a commercial market, Oja-Gbooro, in Ilorin, Kwara State, Nigeria. Enough quantity was purchased at the commencement of the experiment to safeguard fluctuations in quality of this ingredient with different batches because of the inconsistency in processing techniques as noted by Omole and Tewe (1989). The sample was freed of dust particles, air dried and then homogenized using mortar and pestle. The Rice husk was sieved through a 20-mesh sieve stored in a pre-cleaned polyethylene storage bag and kept at a temperature of -5°C in order to suppress fungal growth and minimize change in the quality of samples.

Analytical Reagent:

The reagents used in the course of this research are; n- Hexane, Sodium hydroxide, sodium potassium tartrate, potassium hydroxide, copper sulphate, carbon tetrachloride, 1N HCl, HNO₃, 1.25% H₂ SO₄ and 1.25% NaOH, Concentrated H₂SO₄.

Reagent preparation (Sodium Potassium tartrate):- To a 930 ml of distilled water, 10 ml of 10N potassium hydroxide solution and 20 ml of 25% sodium potassium tartrate solution were added; 40 ml of 4% CuSO₄.5H₂O solution was also added slowly and vigorously stirred.

Extraction of Oil from Rice husk

20 g of Rice husk was weighed into a cellulose thimble (30 mm x 77 mm), and the thimble was placed in a Soxhlet device. 500 mL of n-hexane was used as the extraction solvent and the extraction was performed for 7 hrs. The temperature in the extraction chamber was approximately 62 to 63 °C. The extract was concentrated using simple distillation at the same temperature range. The extraction efficiency of n-hexane and methanol was optimized using this method at different weights of the rice husk.

Proximate Analysis

Moisture Content in rice husk, about 5 g of the rice husks sample was weighed into a porcelain crucible and placed in the oven at temperature of 90-100 °C for 3 to 4 hours. The dried sample was weighed and the weight loss signifies the moisture content and the percentage moisture content was calculated (UCADAVIS, 2000). For the ash content analysis, 2 g of dried rice husks sample was weighed in a porcelain crucible and the crucible placed in a muffle furnace at a temperature of 650°C for 4 hours. After ashing, the ashed rice husk sample was placed in a desiccator to cool before weighing and the percentage of ash content was calculated (Prometheus, 1996).

For protein analysis, 0.5 g of sample was weighed into 80 ml centrifuge tube. 1 ml of carbon tetrachloride was mixed with it and then 50 ml of sodium potassium tartrate was added. It was shaken vigorously for 10 min and allowed to stand for 1 hour and then mixed thoroughly. A portion was transferred to a 20 ml centrifuge tube and centrifuged until it was perfectly clear. The colour intensity was determined at 55 mμ with the aid of spectrophotometer with the indicated reagent as blank.

Crude Fibre, Fat and Carbohydrate Content Determination in Rice Husk

Crude fibre: 2 g of the rice husk sample was defatted with diethyl ether for 8 hours. This was then boiled with 200 ml of 1.25% H₂SO₄ under reflux for 30 minutes. The washed material was boiled with NaOH for exactly 30 minutes and filtered, after which it was dried in an oven at 100°C, cooled and weight. In addition, the fat and carbohydrate content was analysed, 2 g of Rice husks was weighed into a cellulose thimble (30mm x 77 k mm), and the thimble was placed in a Soxhlet device. 500 mL of n-hexane was used as the extraction solvent and the extraction was performed for 7 hrs. The temperature in the extraction chamber was approximately 62 to 63°C. The extract was filtered and the filtrate was distilled to separate the crude oil from the extraction solvent, after which the crude oil was weighed. The carbohydrate content was determined by the subtraction of % protein, % ash, % crude fibre, % moisture, % fat from the entire dry sample.

Silica content determination in rice husk

The silica content of the rice husk was determined by a modified method of Kamath and Proctor (1988). In this method, the husk sample was ashed in a muffle furnace at 650°C for 4 hours. 60 ml portions of 1 N NaOH was added to 10g of the rice husk ash sample and boiled in covered

250 ml Erlenmeyer flasks for 1 hr with constant stirring to dissolve the silica and produce a sodium silicate solution. The solution was filtered through Whatmann No. 41 ashless filter paper, and the carbon residue was washed with 100 ml of boiling water. The filtrates and washing were allowed to cool to room temperature and were then titrated with 1N HCl with constant stirring to pH 7. Silica gels started to precipitate when the pH increased to <10. The silica gels formed were air dried for 18 hr. Deionized water (100 ml) was added to the gels and were broken to make slurry. Slurries were then centrifuged for 15 min at 2500 rpm, the clear supernatants were discarded and the washing step was repeated. The gels were transferred into a beaker and dried at 80°C for 12 hr to produce xerogels. Selected silica xerogel samples were ground and subjected to additional washing with water and dried again after which the dried silica was weighed.

Determination of metal contents of rice husk oil

The oil extracted using n-hexane was weighed into a digestion vessel, 15 ml of HNO₃ and 5 ml of HCl were added into the vessel and then gently swirled. It was then heated using a hot plate for a few minutes and brown fumes was observed. The completion of the digestion is achieved when the brown fumes become white. 20 ml of water was then added to the digest and filtered, after which the filtrate was made up to 250 ml mark and then taken for analysis using Atomic Absorption Spectrophotometer (AAS) (model 210 VGP) (Oluremi *et al.*, 2013).

3. Results and Discussion

The concentration in percentage of moisture obtained from this research was 8.6%. According to Ajayi *et al.* (2012), the percentage of moisture present in rice husk ranges from 8-9%. This shows that this result is in conformity with previous researches. Jeon *et al.* (2012) compared rice husk to general wood biomass containing less than 1 wt. % ash, the rice husk was shown to consist of more than 10 wt. % of ash. The concentration in percentage of ash obtained from this research was 19% (Table 1) which is in conformity with the findings of Oyenuga (1968) who reported that rice husk is composed of 15-22% ash.

Table1: Proximate analysis of rice husk

Constituents	Concentration (%)
Ash	19.000±0.016
Carbohydrate	14.300±0.054
Crude fibre	45.500±0.102
Fat	4.800±0.018
Moisture	8.600±0.117
Protein	7.800±0.140

According to Oyenuga (1968), the concentration of crude fibre in rice husk ranges from 39-42% which may also differ slightly according to some factors such as climatic condition. The concentration in percentage of crude fibre recorded from this work was 45.500%. This shows that the result is in agreement with the findings which have been made by other researchers. The concentration in percentage of fat recorded was 4.800 %, the variation observed in the concentration might be as a result of genotype and environmental differences (Eggum *et al.*, 1982).

According to Ajer *et al.* (2014), there was a comparison between the rice husk of two different regions which are Garko and Kura in Kano State, Nigeria. The concentration of carbohydrate in the rice husk from Garko was 12.860% while that of Kura was 5.900%. The concentration of carbohydrate recorded in this work was 14.300%. Eggum *et al.* (1982), had reported that the variation observed in these results may be due to genotype and environmental differences.

The average % composition of protein was 7.920%. The protein content was determined in six portions of weighed rice husk, the mass ranges from 5 g - 30 g. From this study, it was observed that there is difference in the concentration of protein in the different masses of sample and this reveals that the higher the mass of rice husk, the higher the mass (g) of the protein content.

92% silica content was observed from 10 g of rice husk ash. According to Sarangi *et al.* (2009), silica content in rice husk ash is 87-97%. The presence of high amount of silica makes it a valuable material for use in industrial application. From X-Ray Fluorescence, the result confirmed that the major compound in rice husk ash is silica. (Onojah *et al.*, 2013) Adam *et al.* (2006) also reported that the silica content of the rice husk ash (RHA) can be as high as 90–98%. Hence, the 92% silica recorded during this research is in agreement with earlier findings.

Due to its high silicon content, rice husk has become a source for preparation of elementary silicon and a number of silicon compounds especially silica silicon carbide and silicon nitride (Della *et al.*, 2002). The oil obtained by extraction with n-hexane was analysed with AAS; the results are presented in Table 2.

Table 2: Concentration of minerals in the rice husk oil obtained with n-hexane

Minerals	Concentration (Mg/L)
Calcium	4.190±0.043
Magnesium	0.990±0.027
Potassium	1.310±0.002
Sodium	43.220±0.419
Iron	0.400±0.052
Phosphorus	3.770±0.020

Table 3: Concentration of minerals in vegetable oil

Minerals	Concentration (Mg/L)
Calcium	3.100±0.041
Magnesium	0.840±0.039
Potassium	1.730±0.010
Sodium	44.030±0.089
Iron	0.510±0.006
Phosphorus	3.150±0.031

Comparison between the rice husk oil and the vegetable oil was investigated. It was observed that calcium, magnesium and phosphorus have higher concentration in rice husk oil than in vegetable oil while potassium, sodium and iron have lower concentration in rice husk oil than in vegetable oil as shown in Figure 1.

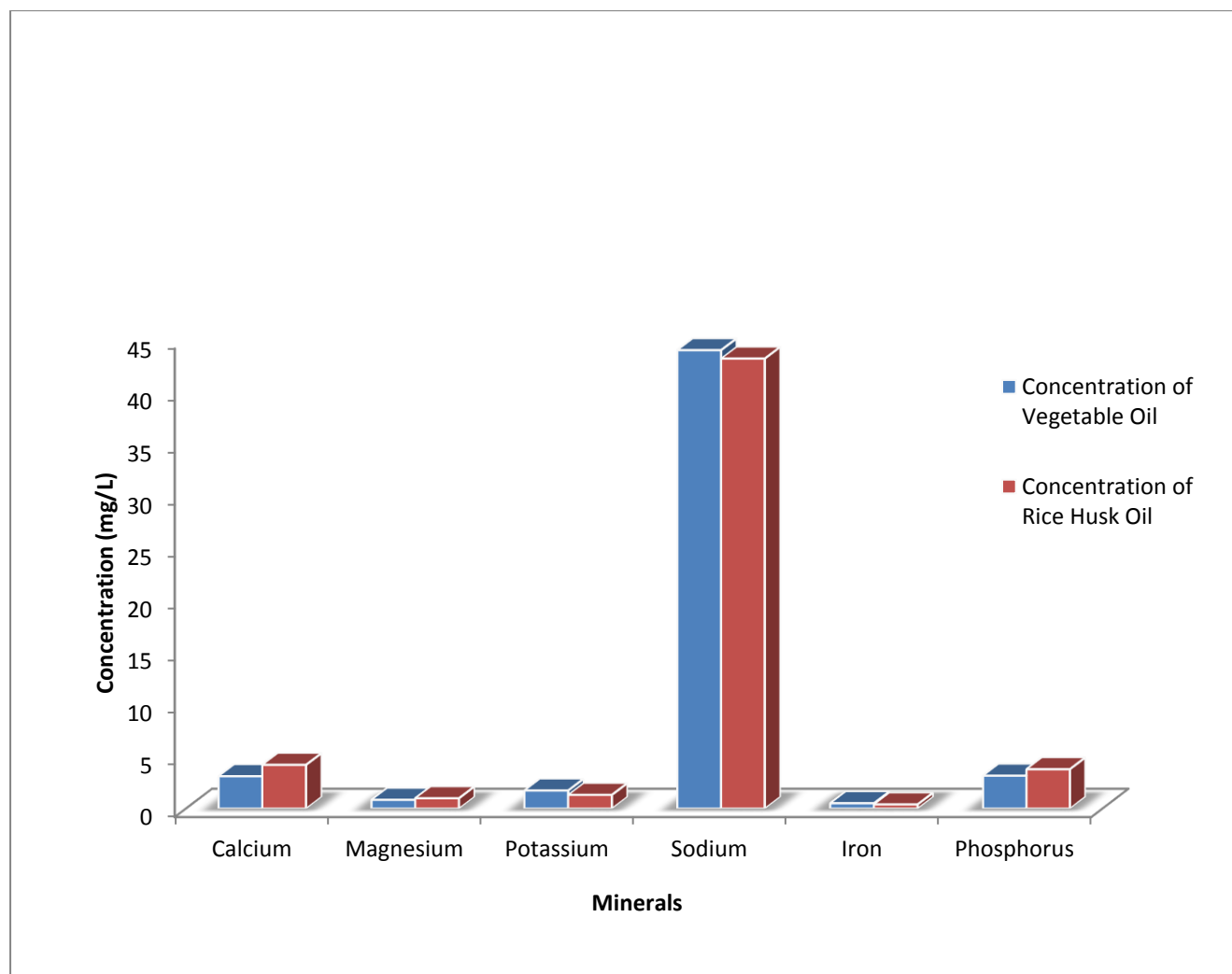


Figure 1: The Bar Chart diagram for the comparison between the minerals in rice husk oil and vegetable oil.

The concentration of calcium in the rice husk oil as shown in Figure 1 was 4.190 mg/l. This is an important mineral which functions as a constituent of bones and teeth, regulation of nerve and muscle function. In blood coagulation, calcium activates the conversion of prothrombin to thrombin and also takes part in milk clotting. It plays a vital role in enzyme activation. Calcium activates a large number of enzymes such as adenosine triphosphatase (ATPase). Very low levels may cause spontaneous discharges of nerve impulses leading to tetany and convulsions (Hays and Swenson, 1985). This means that it has to be high to avoid convulsion.

The concentration of magnesium in the rice husk oil was 0.990 mg/l. It is an active component of several enzyme systems in which thymine pyrophosphate is a co-factor. Oxidative phosphorylation is greatly reduced in the absence of magnesium. Magnesium is also an essential activator for the phosphate- transferring enzymes myokinase, diphosphopyridine nucleotide kinase, and creatine kinase. It also activates pyruvic acid carboxylase, pyruvic acid

oxidase, and the condensing enzymes for the reaction in the citric acid cycle. It is also a constituent of bones, teeth, enzyme co factor, (kinases etc.). The concentration of phosphorus in the rice husk oil as shown in Figure 1 was 3.770 mg/l. Phosphorus in every cell of the body is vitally concerned with many metabolic processes, including those involving the buffers in body fluids (Hays and Swenson, 1985). It functions as a constituent of bones, teeth, adenosine triphosphate (ATP), phosphorylated metabolic intermediate and nucleic acids. It serves as buffering actions i.e. phosphate buffers, functions in the formation of high energy compounds, i.e., adenosine triphosphate (ATP) and also involved in the system. It is observed that calcium, magnesium and phosphorus are very important to human beings for the bones, teeth and syntheses of phospholipids and phosphor-proteins.

The concentration of potassium in the rice husk oil as shown in Figure 1 is 1.310 mg/l. It is the principal cation in intracellular fluid and functions in the balancing of acid-base regulation of osmotic pressure, conduction of nerve impulse and muscle contraction particularly the cardiac muscle. Potassium is also required during glycogenesis (Hays and Swenson, 1985). Sources include Table salt and drinking water. The charges in osmotic pressure are largely dependent on sodium concentration (Hays and Swenson, 1985). The concentration of sodium in the rice husk oil was 43.220 mg/l. It is the principal cation in extracellular fluids and it also regulates plasma volume and acid-base balance, is involved in the maintenance of osmotic pressure of the body fluids and preserves normal irritability of muscles and cell permeability.

Smouse (1994) reported that for the best stability of oils, the level of iron should be between 0.100 mg/L to 0.400 mg/L, this will enhance the stability and edibility of the oil and the prolongation of the shelf life. The concentration of iron in this research for rice husk oil was 0.400 mg/L and 0.510 mg/L in the vegetable oil (Table 3), respectively. Thus, oil that was extracted from rice husk is of better edibility than that of vegetable oil. According to Farooq *et al.* (2004) metals such as iron are known for oxidative activities in fats and oil at low concentration.

4. Conclusion

Utilization of rice husk could solve the disposal problem and reduce the cost of waste treatment. Mineral profile of rice husk oil showed that it is good for consumption because of its high concentration of calcium, magnesium and phosphorus content if well refined and therefore serves as an alternative to conventional oils such as vegetable oil in domestic stores. The rice

husk oil has the potential for both domestic and industrial use provided it is well refined and taken care of through industrial process. Both n-hexane and isopropanol did extract oil from the rice bran. N-Hexane when compared to isopropanol gave more extraction yield than isopropanol but with little significant difference.

The two solvents can thus be used to extract oil from rice bran. Multiple benefits of rice husk and rice husk ash can be achieved by future critical research efforts to provide new impetus for local and regional sustainable development. In this research, it has been discovered that, rice husk oil (oil extract from rice husk) is a good edible source of oil which is very nutritious to the human body, it is higher in body building minerals (bones and teeth) such as calcium, magnesium, and phosphorus than vegetable oil. Therefore, it is recommended for consumption. Government should help to make an awareness of the benefits that can be derived from rice husk and its oil and it should be made known to the society that many of the things we regard as wastes are not actually wastes and they can be recycled and refined for the benefit of society.

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