DETERMINATION OF METAL CONTENT AND AN ASSESSMENT OF THE POTENTIAL USE OF WASTE CASHEW NUT ASH (CNSA) AS A SOURCE FOR POTASH PRODUCTION

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The potential use of waste cashew nut shell (CNS) ash as a source for potash production was investigated in this study. Managing waste ash generated from cashew nut processing is a major challenge, as land filling and open dumping of the waste ashes have been the main options in management of the ash in Nigeria. Economically viable ways of using waste ash rather than having to dispose of it have to be investigated. The CNS was air-dried for 4 weeks and combusted to ashes; the resulting ash was extracted with water for its potash content. Some parameters of the CNS, including moisture, dry matter, and ash content, were determined. Potash yield obtained was 33.4% of 150 g CNS ash used; analysis of the potash gave it a percentage purity of 78%, while purity on recrystalization increased to 86%. Potash yield from CNS ash was comparable to those reported for wood ash, plantain peels, and other agro-wastes. Also, the results showed that the CNS shared similar lignocellulosic properties and characteristics with hardwood biomass.

Keywords: Ash; Alkali; Potash; Cashew nut shell

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INTRODUCTION

Cashew (*Anacardium occidentale*) is one of the Nigeria's leading cash crops, being the world's 2nd largest producer of cashew. Nigeria produces 636,000 tons of cashew nuts yearly (FAO, 2008), most of which is for the export market. The cashew nuts are exported either as whole shell or they are processed; and the cashew kernel is exported. Agricultural and agro-industrial waste accumulates as a result of the activities of cashew processing industries; this is largely due to the location of such industries near the raw materials, and the location of farms and plantations in rural areas. This contributes to the present problems of environmental pollution, as government attention is mostly focused on cities and towns. Agro-waste or plant biomasses in Nigeria are mostly subjected to open-air burning with its attendant environmental implications (Babayemi and Dauda 2009). These wastes could be efficiently managed if used for other viable industrial, agricultural, or domestic purposes, thereby reducing the problem of environmental pollution and also creating wealth.

Cashew processing industries generate the cashew nut shell as a waste product; they utilize the waste cashew nut shell as a source of heat, especially in Nigeria where the

public energy supply is erratic and dependence on diesel fuel is costly. The perennial nature of the crop means that there is an abundance of waste cashew nut shell at the peak of the season; most processing industries resort to dumping of the excess waste cashew nut shell on open land and indiscriminate burning. Use of plant biomass as source of energy offers a cheap, environmentally friendly alternative to the conventional petroleum energy sources. Energy generation from biomass such as tree bark, wood residues, and other plant materials produces a considerable amount of fly and bottom ashes. Managing waste ash generated from cashew nut processing is a major challenge, as land filling and open dumping are the main options in management of the waste ash.

It was reported that potash production provided early North American settlers with the badly needed cash as they cleared their wooded land for crop production and cleared tree stumps. The cleared wood needed to be disposed of, and the easiest way to accomplish this was to burn any wood not needed for fuel or construction. Ashes from hardwood trees could then be used to make lye, which could be used to make soap or boiled down to produce valuable potash. Exploration of ash-derived alkalis for domestic use is an ancient craft (Onyegbado et al. 2002; Nwoko 1982) involving simple technology and chemistry (Babayemi et al. 2010a). The general principles in potash production from ashes involved leaching the ashes with water; the 'leachate' is then evaporated. The residue is the crude potash. The quality of the residue depends on the materials used, as well as procedure and equipment. Babayemi et al. (2010a) report the details. Materials for ashes in potash production such as wood (Adewuyi et al. 2008; Babayemi and Adewuyi 2010), banana and plantain peels (Babayemi et al. 2010b; Onyegbado et al. 2002; Ankrah 1974), cocoa pod husk (Afrane 1992), palm bunch (Kuye and Okorie 1990), cassava peels (Onyekwere 1996), and livestock dung (Babayemi et al. 2010c) have been investigated. The limitations to the use of some of these materials include low potash yield. Furthermore, some of those which give high potash yield are not available throughout the year.

Economically viable ways of using waste ash rather than having to dispose of it have to be investigated. There is already a vast body of information on utilization of fly ash (FA) in building/construction, production of aggregates and more recently for agriculture (Brian et al. 2003).

This study therefore seeks to find potential use for waste ash residue of cashew nut shell (CNS) as a source of potash.

EXPERIMENTAL

Sample Collection and Treatment

The CNS, which were not yet burnt, were collected at a point from the dump site of a cashew nut processing plant in Olowopokun, Iseyin, Nigeria. The waste CNS was sun-dried for 4 weeks, and then ashed.

Determination of Moisture Content (MC), Dry Matter Content (DM) and Density of the Samples (DS)

A known weight (W_1) of air-dried cashew nut shell sample was taken and oven-

dried at 105 ^{o}C for 3 hours (Radojevic and Bashkin 2005). It was transferred into a desicator to cool and then weighed (W_2). Calculations were carried out as follows,

$$MC = [(W_1 - W_2) / W_1] \text{ X } 100 \% \quad (1)$$

$$DM = (W_2 / W_1) \text{ X } 100 \% \quad (2)$$

$$DS = (W_2 / V_1) \text{ (gmL}^{-1}) \quad (3)$$

where V_1 is the volume of quantity of (W_2) determined. Duplicate determinations were carried out.

Ash Content (*AC*), Loss in Weight (*LW*), and Density of Ashes (*DA*)

A known weight (W_3) of sample dried in the oven at 105 ^{o}C for 3 hours was combusted to ashes in a muffle furnace set at 500 ^{o}C for 4 hours using porcelain crucibles. After cooling, the weight (W_4) of the ash residue was determined. The density of the ashes was determined with slight modification to GEA Niro Method No. A 2a (2006). The ash content was calculated using the following relationship,

$$AC = (W_4 / W_3) \text{ X } 100 \% \quad (4)$$

$$LW = [(W_3 - W_4) / W_3] \quad (5)$$

$$DA = (W_5 / V_2) \text{ (gmL}^{-1}) \quad (6)$$

where V_2 is the volume of the quantity of ash (W_5). Duplicate determinations were carried out.

Extraction of Alkali from the Ash

The method used followed that described by Adewuyi et al. (2008) in which both high quality and quantity of potash were said to be obtained, and the effectiveness of the method was comparable to other existing ones. 150 g of the waste CNS ash sample were placed in a 4-litre transparent plastic bottle. Two litres of distilled water were added; the mixture was covered and thoroughly shaken. It was allowed to stand for about 12 hours, hanging on a clamp on a retort stand. The lid was removed and a few pin holes were made at the bottom of the bottle using an injection needle. The extract solution leaked into a collecting bowl as it filtered through the ash sediment. 1.5 litres of the extract solution was evaporated to a smaller volume and then quantitatively transferred into a pre-weighted crucible in which evaporation to dryness was carried out. The crucible with its content was placed in the oven set at 105 ^{o}C for 3 hours. After cooling in a desicator, the weight (W_6) of the potash in the crucible was determined using a Mettler balance.

The actual amount of potash from the 150 g of ashes was calculated as follows: 1.5 litre of extract solution contained W_6, then 2 litres of extract solution would contain $[(W_6 X 2)/1.5]$g = z (g). Therefore, the percent potash yield is given by (z/150) X 100. Duplicate determination was carried out.

Determination of Purity of the Crude Potash

3.45 g of the crude potash were dissolved in water and made up to mark in a 250 mL standard flask. 10 mL was pipetted into a conical flask and then titrated with 0.1M hydrochloric acid, using methyl orange as indicator (Babayemi et al. 2010a). Five replicates were obtained, and duplicate analysis was carried out. The chemical reaction could be shown as:

$$2\ HCl\ (aq) + K_2CO_3\ (aq) \rightarrow 2\ KCl\ (aq) + CO_2\ (g) + H_2O\ (l) \quad (7)$$

Analysis of Carbonate and Hydroxide Content

A double-indicator method was used in the acid-base titration analysis of the mixture of alkali hydroxide and carbonate (Ojokuku 2001). 10 mL of the sample solution was pipetted into a conical flask, 2 drops of phenolphthalein indicator was added, and the mixture was titrated with 0.1M HCl until a colourless solution was obtained. At that point, the whole of the hydroxide and half of the carbonates had been titrated, giving a burette reading v_1. The equation of the reaction is as shown below:

$$HCl\ (aq) + KOH\ (aq) \rightarrow KCl(aq) + H_2O\ (l) \quad (8)$$

$$HCl\ (aq) + K_2CO_3\ (aq) \rightarrow KCl(aq) + KHCO_3\ (aq) \quad (9)$$

Methyl orange was added to the resulting colourless solution and titrated until the colour changed from yellow to orange. At that point, the remaining bicarbonate was neutralized by the acid; the burette reading now becomes v_2. The equation of the reaction is as follows:

$$HCl\ (aq) + KHCO_3\ (aq) \rightarrow KCl(aq) + H_2O\ (l) + CO_2\ (g) \quad (10)$$

Calculations:

Titre for neutralization of $KHCO_3$ = v_2-v_1
Titre for neutralization of KOH = $v_1 - (v_2$-$v_1)$
Titre for neutralization of $K_2CO_3 = 2(v_2$-$v_1)$

Assuming the average titre for neutralization of KOH, v_1- (v_2-v_1) = x mL, and that of K_2CO_3, $2(v_2$-$v_1) = y$ mL, then the molar concentration of KOH = 0.1 X x

Therefore,

$$KOH = [\ 0.56\ x\ /\ (0.56\ x + 0.69\ y)\ ]\ X\ 100\ \% \quad (11)$$

and

$$K_2CO_3 = [\ 0.56\ y\ /\ (0.56\ x + 0.69\ y)\ ]\ X\ 100\ \% \quad (12)$$

The Amount of KOH, K_2CO_3, and Non-Alkali Contents

The amount of KOH, K_2CO_3, and non-alkaline contents of the crude potash were calculated as follows:

$$\% \text{ KOH} = t \text{ X } \% \text{ Purity of crude potash} \quad (13)$$

$$\% \text{ } K_2CO_3 = u \text{ X } \% \text{ Purity of crude potash} \quad (14)$$

$$\% \text{ Non- alkali contents} = 100 - \% \text{ Purity of crude potash} \quad (15)$$

where t and u are the percentages of KOH compared to K_2CO_3 and percentage of K_2CO_3 compared to KOH, respectively.

Purification of Crude Potash

The crude potash was re-dissolved in sufficient distilled water and heated gently until there was an appearance of precipitates, and then allowed to cool to room temperature. The less soluble components crystallized out on cooling; the remaining solution was decanted off and evaporated to dryness and finally to constant weight. The dried crystals were subjected to titrimetric analysis to determine the purity (Adewuyi et al. 2008).

Analysis of Inorganic Elements

1g of ground sample was weighed and placed in a beaker. 30 ml of 1:1 HNO_3 (10 mL water + 10 mL concentrated HNO_3) were added and boiled gently on a hotplate until the volume was reduced to approximately 5 mL while stirring. A further 10 mL of 1:1 HNO_3 were added and the process repeated, it was cooled and the extract filtered through a Whatman no. 41 filter paper, and the filter paper and beaker were washed with successive 0.25M HNO_3 portions. The filtrate was transferred to a 50 mL volumetric flask and diluted to the mark with de-ionised water. The sample was analyzed by atomic absorption spectroscopy (Radojevic and Bashkin 2005) at 228.8 nm, 357.9 nm, 283.3 nm, 324.7 nm, 248.3 nm, 213.9 nm, 422.7 nm, 766.5 nm, 285.2 nm, and 589.0 nm for Cd, Cr, Pb, Cu, Fe, Zn, Ca, K, Mg, and Na, respectively.

RESULTS AND DISCUSSION

Table 1 shows the moisture (*MC*) (12.4 %), dry matter (*DM*) (87.6 %), ash (*AC*) (3.00±0.46 %), and potash (*PC*) (33.4±0.22 %) contents, as well as the densities (*DS*) (0.34 g/mL) of the CNS and of the resulting ash (*DA*) (0.26 g/mL). The results of the titrimetry are shown in Table 2: the initial purity was 78% with the impurity (non-alkali) content of 22%; and the final purity after recrystallization was 86% with an impurity (non-alkali) content of 14%.

The amount of KOH (1.60 %) compared to K_2CO_3 (98.4 %) are shown in Table 3, while Table 4 shows the results of metal analysis.

Table 1. Physical Parameters, Ash, and Potash Contents of CNS

Parameters	Value
MC (%w/w)	12.4
DM (%w/w)	88.6
DS (g/mL)	0.34
DA (g/mL)	0.26
LW (%w/w)	97.0
AC (%)	3.00±0.46*
PC (%)	33.4±0.22*
MC: moisture content; DM: dry matter content; DS: density of sample; DA: density of ash; LW: loss in weight. ±SD*, n = 4	

From the results of the physical parameters, one may infer that CNS shares similar characteristics with hardwood biomass (Bingh 2004). Ash yield was low, as is usually the case with most woody biomass, and this explains why a large quantity of CNS yielded only little quantity of ash. Potash yield was moderate, but higher than those (2.77 to 26.88%) reported for several African wood species (Adewuyi et al. 2008). The percentage purity (78%) determined for CNSA here is high, compared with those reported in the literature: 12.40 to 56.73 % for various agro-wastes (Taiwo and Osinowo 2008), 4.50 to 95.50 % for wood species (Adewuyi et al. 2008), and 69.00 to 81.90 % for musa species (Babayemi et al. 2010b); however, the value falls within the range of those in the references. There was an increase in purity on recrystalization (from 78 to 86 %). The result of duplicate analysis showed no significant difference: *t*-calculated = 3.464 while the critical value = 4.520 at 95 % confidence level.

Table 2: Average Titre Value, Concentration and Purity of Crude Potash and Purity on Recrystalization.

Average titre (mL)	Concentration (mol/dm^3)	Purity (%)	Non-alkali (%)
14.1	7.84×10^{-2}	78	22
RECRYSTALIZATION			
18.2	0.09	86	14

The higher amount of K_2CO_3 compared to KOH suggests that the potash obtained was predominantly potassium carbonate. However, the significant amount of soluble non-alkali content observed implies the presence of other soluble salts than K_2CO_3.

Table 3. Amount of KOH Compared to K_2CO_3 Expressed as a Percentage

	KOH (%)	K_2CO_3 (%)
CNS Ash	1.60	98.4

In the results of analysis of heavy metals (Cd, Cr, Pb, Cu, Fe, and Zn), Fe had the highest value (7937 mg/kg), while Cd showed the least concentration (1.5 mg/kg). Macro-element analysis of the CNS ash (Ca, K, Mg, and Na) indicated the least concentration of 1.8 g/kg for Na, while Ca had the highest (38.7 g/kg). Generally, the values were higher than those in the references (Misra et al. 1993; Babayemi et al. 2010b), perhaps because this is a different species of plant, and analyzing the nut in particular.

Table 4. Concentrations of Nutrient and Heavy Metals in CNS Ash

Heavy metals (mg/kg)	
Cd	1.50 ± 0.01
Cr	53.1 ± 0.14
Pb	142 ± 0.26
Cu	80.4 ± 0.16
Fe	7940 ± 5.00
Zn	726 ± 1.16
Nutrients (g/kg)	
Ca	38.7
K	2.70
Mg	2.20
Na	1.80
Triplicate analysis (±SD, n = 3)	

CONCLUSIONS

1. The high potash yield of the cashew nut shell shows that it has a potential use as a source of materials for potash production; and there is the possibility of improving the purity of the potash by recrystalization.
2. However, bioaccumulation of heavy metals in the plant may be inferred, and this perhaps may have effects on the chemistry of potash arising from this source. Further work is suggested to verify this.

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