# PRODUCTION AND CHARACTERIZATION OF POTASH FROM MAIZE STOVERS ASH BY NEUTRON ACTIVATION ANALYSIS AND X-RAY DIFFRACTION

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## ABSTRACT

The production of potash from maize Stover's ash via the traditional simple technology and its characteristic analysis using Neutron Activated Analysis (NAA) and X-ray Diffraction (XRD) analysis have been studied. Thermal combustion of maize stover on the farm land has created much pollution in the environment couple with destruction on soil nutrients on the farm land. So many problems have also emerged from potash mining, like reduction in farm land, flooding and huge cost of beneficiation, leading to high cost of potash. Production of potash from maize stover ash is another source of wealth generation and waste management disposal system, providing environmental cleanliness. In light of the global high demand for potash usage, potash from maize stover (MSAP) can close-up the gap since maize crop is produced annually all over the world more than any other grain to the tune of about 785 million tons, which determines the total amount of wastes generated by the crop after the grains have been harvested. The analysis of MSAP conducted showed the qualitative and quantitative value of potash as an eutectic mixture of potassium and other elements, with potassium accounting for 50.75%, chloride 29.10%, calcium 0.6%, sodium 0.03% and manganese 9.04%, while the XRD showed that the MSAP has unique compositions such as Ca, Cl, Na, and Mn that formed the eutectic mixtures of Sylvite syn (KCl.Ca), Sodium Potassium Chloride (Na.K.Cl), Calcium Chloride ($CaCl_2$), and Hydrophilte, syn ($CaCl_2$). This study has shown that the NAA and XRD analyses of MSAP salt produced from the ash of maize plant in a controlled atmosphere of $550^oC$ results to potassium salt with chlorides of K, Na and Ca as a double salt for various applications.

**Keywords**: Ash, maize stover, MSAP, NAA, potash, XRD,
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## INTRODUCTION

Potash production has existed for ages before 1790 in the U.S.A, and its demands are increasing daily in the recent years for various applications [1]. Potash denotes a variety of mined and manufactured inorganic crystalline salts having potassium as its major component [2, 3] with a wide area of applications stemming from house-hold uses, agricultural applications to industrial uses [4]. In place of common salt, potash is being used for food seasoning and condiments and has also been found to give relief to hypertensive patients [5]. On the farm, potash is one of the sources of fertilizer and animal feed production; while in the industries, potash is used for making products such as soaps, glass, baked goods and gunpowder [1], brewing beer, textiles, catalyst for synthetic rubber manufacturing, and pharmaceuticals uses [4]. Potash usage covers other areas of discipline such as Aluminum recycling, metal electroplating, snow and ice melting, making of glasses for television and computer monitor, drilling of oil well mud, and water softening to mention but a few [3].

Traditionally, the production of potash started with the thermal combustion of wood (typically hardwood) into ashes. The ashes are soaked in a pot of water and then leached to produce lye (filtrate). The filtrate is used for products manufacture or is further processed by evaporating (or by boiling) it to produce potash [6]. Since 1790, this method of potash production has not met global needs of potash, which led to large scale mining of potash from the soil [1]. However, Potash mining has introduced so many problems among which include environmental degradation, reduction in farm lands and flooding which have reduced capacity of farm production and pushing prices higher [3]. In addition to this, mined ore requires a whole lot of beneficiation that includes material separation, size reduction, compaction granulation and drying, adding to the cost of potash production [1]. In spite of global potash production through mining of ores [3, 8] as shown in Table 1, demands for potash are increasing daily [1]. These called for reasons why there is need to find other ways to increase potash production using agricultural wastes that are in abundance, which are other potential sources of potash production. To this end, maize stover ash (MSA) is being considered as another area of interest for potash production in addition to mining, since maize farming is huge across the globe and in Nigeria only, maize production ranges in tune of 8 metric tons/annum [7].

**Table 1**: Quantity of potash produced by various countries

| Countries | Quantity of potash Produced (Mt/yr.) |
|---|---|
| **Germany** | 38 |
| **Belarus** | 8.5 |
| **Russia in Uralkali** | 7 |
| **Ust-Yaivinski** | 4 |
| **China** | 3.5 |
| **Jordan** | 3 |
| **Canada** | 1.1 |
| **Brazil** | 1 |
| **Congo Brazzaville** | 0.5 |

Source: [3].

All over the world, farming is a global noble profession that is being practiced to provide sustainable food for the populace. The waste products generated in farming is enormous leading to millions of metric tons needed to be properly disposed of by waste management systems, such as landfill or conversion into fly ash through thermal combustion [9]. The disposal of these agricultural wastes mostly drain resources and nutrient through land depletion, in addition to being hazardous to the environment causing greenhouse warming, most especially when combusted without proper control. Meanwhile, if the wastes are converted into useful materials, they could be sources of wealth creation in addition to providing a cleaner environment. Though, it has been reported that burning of hard wood into ashes was the source of alkaline for the production of potash in its early days [6], recently, potash is being derived from ashes of plants wastes such as rice husk, saw dust, banana peels, etc., in varying quantities [10, 11]. It was reported according to the Australian Standards on potash (EN 15297 and EN 15290) that potash consists of both minor and major elements of which K, Ca, Si, Na, and P are the major elements [13]. The interaction phases of the minerals present in potash is predicated on the geological location of the mined ore or the type of plant from which the ash is derived [11]. It has been observed that most mined potash comes from the mineral sylvite (KCl), sulphate of potash (SOP or $K_2SO_4$) [14], a mixture of KCl and NaCl (halite), etc. [3]. In addition to these products, a good quality of potash with naturally combined eutectic mixture of salts could be derived from the ashes of plants like maize stover.

Maize or "Zea-mays" also known in some English-speaking countries as corn, is a large grain plant domesticated by indigenous people in Mesoamerica in prehistoric times [15]. The name was coined by Carl Von Linne, and was derived from a Greek word and it is said that the meaning of the name is "preserver of life". It belongs to the kingdom Plantae, order Poales, family of Poaceae and genus Zea. The leafy stalk produces ears which contain the cobs that produces the grain and after the removal of the grains the left over plant is popularly called Stover, which consists of the stalk and leaves as agricultural wastes [15]. All over the world, maize crop is produced annually more than any other grain [16]. Worldwide production of maize is about 785 million tons, and in Nigeria maize production is nearly 8 million tons per annum [7] of which Plataeu, Kano, Kaduna, Sokoto, Gombe, Bauchi, Zamfara, Benue, Kogi, Nassarawa and Taraba contribute the major percentages [17]. The total land area where maize is planted is above 2.5 million hectares with an estimated yield of about 1.4 metric tons per hectare, and the harvest of maize occupies the second place of production, after sugar cane, and first within cereals [12]. This increasing level of production is due to an increase of cultivated areas which determines the total amount of wastes generated by the crop after the grains have been harvested. Maize stover, universally appears as waste material after harvesting of the maize crop. Most time the waste is usually burnt on the farm land as means of waste disposal that comes with its own problems like environmental pollution and land depletion [9]. In light of environmental protection and material recycling viewpoints, there is an increasing need to maximize the use of these wastes maize stover for other purposes such as conversion into potash that is in a great demand.

The maize stover ash is an inorganic mineral residue collected from the incineration of organic agricultural wastes [18]. The potash extracted from the ash is meant to be hydroxides of alkali metals (Na or/and K), but in most cases, it could contain other water-soluble non-alkali substances such as chloride and sulphate salts [11]. In some instances, ashing in the open atmosphere may contain some minimum amount of carbon due to incomplete combustion of the plants which also reduces the ash yield; but for total ash determinations, ashing devoid of carbon is completed in a muffle furnace with a controlled temperature ranging from 400°C to 700°C, but 550°C is most satisfactory to avoid loss of important elements [18].

## MATERIALS AND METHODS

The production of potash (MSAP) from maize stover ash was achieved by collecting about 23Kg of maize stover (Agricultural wastes) from a maize farm at Industrial Development Centre (IDC), Samaru in Sabon Gari local government area, Zaria, Kaduna State. After post harvesting of the maize and sun drying the stover to a constant weight, they were milled into small sizes of 2000µm using a hammer mill. The milled stover was packed into a head pan and was pre-burnt in a muffle furnace at 600°C for 30 minutes to decarbonize and reduce its sooth. After the sooth had disappeared, the stover was finally activated at 550$^{o}$C holding it for 1 hour for complete combustion into ashes to prevent the mineral contents from being lost. The lumps in the ashes were removed to increase the surface area and 5Kg of ashes were recovered. The ashes were later dissolved and soaked in a tap water, and leached to obtain an alkali (filtrate). The extraction of the alkaline was done using a 63µm sieve size. The container for the collection of the alkaline requires careful selection since alkali attacks material such as aluminum [9], to this end, a metallic basin container was setup in Plates I(a). The basin was perforated at the base and a layer of 63µm sieve was spread in the basin. The filtrate gradually leached and drips into a collector at the base of the basin forming the alkaline. More water was added continuously until the ash was fully leached and its colour starts changing from deep brown to colourless. The brown coloured filtrate was collected in a plastic bucket Plate I(b).

### Precipitation of potash

The alkaline (filtrate) collected was later boiled and evaporated at 100$^{o}$C, Plate II (a), until some crystal precipitates were formed Plate 2(b), termed the "potash" [Maize Stover Ash Potash (MSAP)]. This was cast into solid brownish tablets Plate III.


**Plate I:** (a) soaked ash


(b) alkaline water collected


**Plate II**: (a) Evaporation of alkaline water


**Plate II:** (b) Formation of potash (MSAP)

**Plate III:** Cast tablet of potash (MSAP)

### Analysis of MSAP by neutron activation analysis (NAA)

The qualitative and quantitative analysis of the MSAP was conducted using Neutron Activation Analysis (NAA) at the Centre for Energy Research and Training, Ahmadu Bello University, Zaria using Nigerian Research Reactor-1 (NRR-1), model MNSR, 2004. The sample of MSAP was placed in the column and an electron beam impinges on an anode generating X-rays in the column. The energy was transferred to the sample and electrons were removed from the innermost shells of the atoms. The energy of the resulting x-rays was used to identify the element(s) and the intensity of the emitted x-rays was used to determine the abundance of the element(s) in the long and short runs.

**Analysis of msap by x-ray refractive diffractometer (XRD)**

The XRD analysis of MSAP was carried out with PANalytical X'pert Pro Mrd PW2040 XRD diffractometer at Tshwane University of Technology, Pretoria in South Africa. The XRD was used to determine the empirical formula, chemical formula and mineral type contained in MSAP compound. The scan range used was from $10^o$ - $80^o$ and $2.0^o$/min scanning rate. Sample of the MSAP (1g) was prepared and placed in a sample holder and placed in the scanner. The results were presented as peak positions at 2θ and x-ray counts in the form of a spectra that reveals the compound's name, mineral name, chemical formula, empirical formula, d-spacing and the ICSD with the crystallographic parameters.

## RESULTS AND DISCUSSION

Table 2 and Figure1 show the results of the qualitative and quantitative analysis of the MSAP using Neutron Activated Analysis (NAA). Table 2 revealed the percentage concentration of the elements present in Maize Stover Ash Potash (MSAP) as a combined mixture of potassium, calcium, sodium, chlorine and manganese, while Figure 1 is the graphical display of elements present in MSAP.

**Table 2:** Percentage classification of elements in MSA potash

| S/No | Items | Elements | NAA (%) |
|---|---|---|---|
| **1** | Potassium | K | 50.75 |
| **2** | Calcium | Ca | 0.60 |
| **3** | Sodium | Na | 0.03 |
| **4** | Chlorine | Cl | 29.10 |
| **5** | Manganese | Mn | 9.04 |
| **6** | Others | BDL | BDL |

BDL = Below detection limit

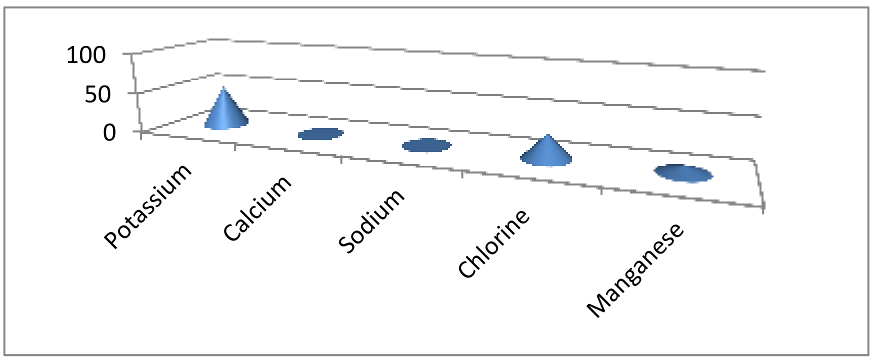


Figure 1: Graphical display of elements present in MSAP.

The potassium has 50.75% concentration, sodium 0.03%, calcium 0.60%, chloride 29.10% and manganese 9.04% respectively. The other insignificant elements such as Si, V, Zn, P, Mg, Al, etc., [13] were seen as traces and were recorded as below detection limit (BDL), these accounted for the balance of the elements. The BDL elements have no reaction with this sample analysed and therefore could not be considered as effective. The analysis of the composition of MSAP showed that it is a potassium based salt having other alkali metals (Na, Ca,) in its composition as eutectic mixtures. Though, sodium has a low level of concentration, but due to its reactivity, it cannot be easily displaced. It therefore has an active role to play in the MSAP which makes the compound a unique one.

**Quality characterization of MSAP by XRD.**

From the XRD analysis of MSAP, Figures 2 and 3 are the spectrum for the chemical formula and compound name for the MSAP. The spectrum revealed that the potash produced after thermal combustion of maize stover into ashes at a controlled atmospheric temperature of 550°C in a muffle furnace, contains different phases of minerals.

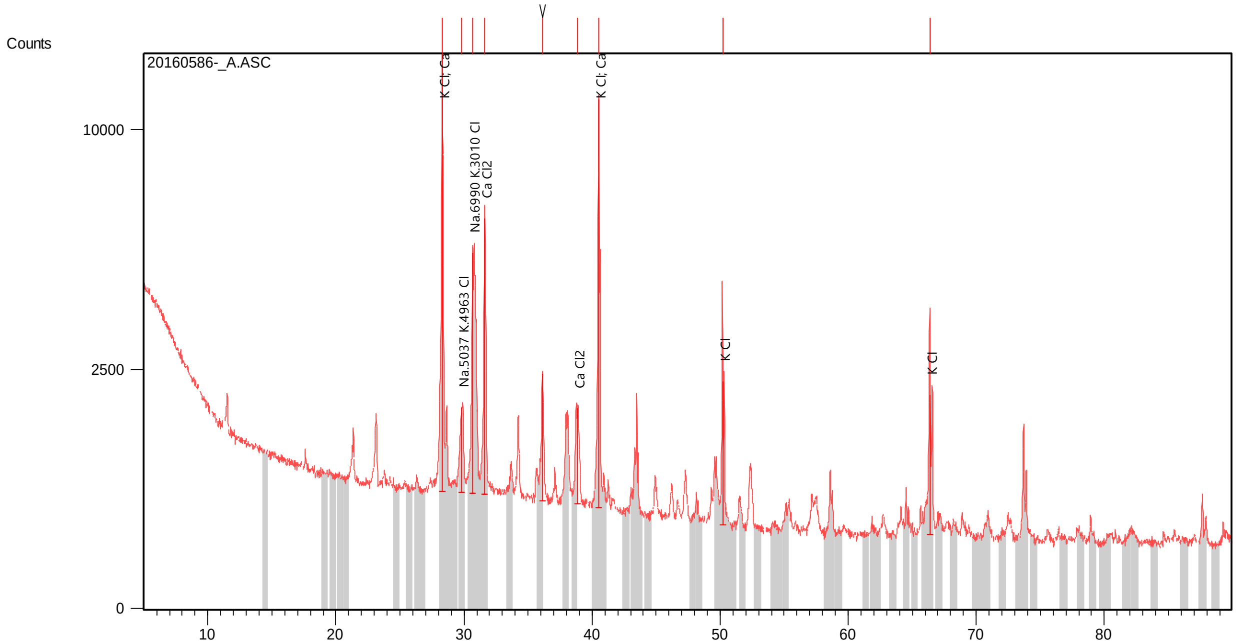


**Figure 2**: MSAP XRD Spectra: chemical formula.

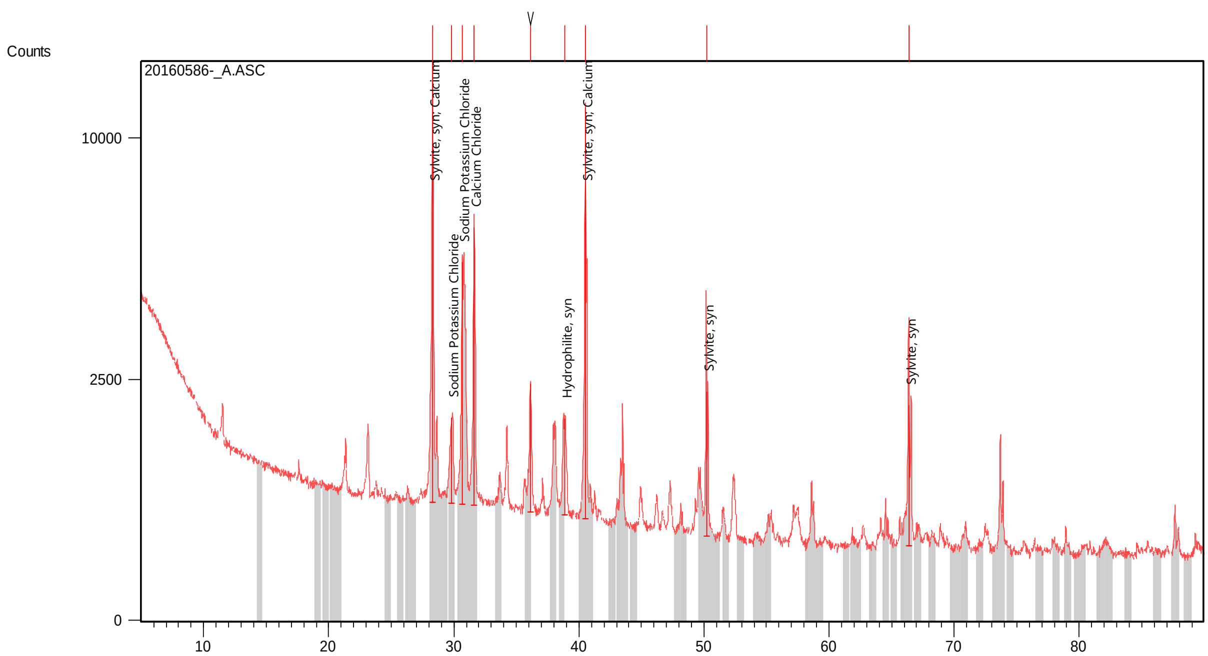


**Figure 3**: MSAP XRD Spectra: Compound name.

It was observed from Table 3, that for the MSAP sample, the major diffraction peaks are 28.29$^o$, 29.85$^o$, 30.69$^o$, 31.64$^o$, 38.84$^o$ and 40.52$^o$ and their inter-planar distances are 3.15Ǻ, 3.00Ǻ, 2.91Ǻ, 2.83Ǻ, 2.32Ǻ and 2.22Ǻ respectively. The relative intensities of the X-ray scattering are 100.00, 9.19, 38.14, 46.96, 9.92, and 83.90 respectively. Their phases at these peaks after matching and relating them with the data base of the XRD programme are detailed in Table 4 as Sylvite, syn (KCl.Ca), Sodium Potassium Chloride (Na.K.Cl), Sodium Potassium Chloride (Na.K.Cl), Calcium Chloride ($CaCl_2$), Hydrophilte, syn ($CaCl_2$), and Sylvite, syn (KCl.Ca) respectively.

**Table 3:** Peak list of sample A

| Pos. [°2Th.] | Height [cts] | FWHM [°2Th.] | d-spacing [Å] | Rel. Int. [%] | Tip width [°2Th.] | Matched by |
|---|---|---|---|---|---|---|
| **28.2891** | 12954.28 | 0.0836 | 3.15481 | 100.00 | 0.0850 | 04-0587; 10-0348 |
| **29.8463** | 1191.10 | 0.2676 | 2.99366 | 9.19 | 0.2720 | 75-0301 |
| **30.6871** | 4941.14 | 0.1673 | 2.91352 | 38.14 | 0.1700 | 75-0303 |
| **31.6364** | 6082.98 | 0.1338 | 2.82824 | 46.96 | 0.1360 | 49-1092 |
| **36.1349** | 1901.19 | 0.1673 | 2.48580 | 14.68 | 0.1700 | |
| **38.8403** | 1284.50 | 0.3346 | 2.31866 | 9.92 | 0.3400 | 01-0338 |
| **40.5194** | 10868.06 | 0.0669 | 2.22637 | 83.90 | 0.0680 | 04-0587; 10-0348 |
| **50.2182** | 1945.81 | 0.2007 | 1.81678 | 15.02 | 0.2040 | 04-0587 |
| **66.4042** | 1769.73 | 0.4896 | 1.40670 | 13.66 | 0.4080 | 04-0587 |

1 Å = $1x10^{-10}$m

**Table 4:** Identified patterns list of the XRD of sample A

| Ref. Code | Score | Compound name | Displacement [°2Th.] | Scale factor | Chemical formula |
|---|---|---|---|---|---|
| **04-0587** | 77 | Sylvite, syn | 0.000 | 1.080 | K Cl.Ca |
| **75-0301** | 30 | Sodium Potassium Chloride | 0.000 | 0.046 | Na.5037 K.4963 Cl |
| **75-0303** | 27 | Sodium Potassium Chloride | 0.000 | 0.028 | Na.6990 K.3010 Cl |
| **75-0297** | 26 | Sodium Potassium Chloride | 0.000 | 0.058 | Na.1002 K.8998 Cl |
| **49-1092** | 21 | Calcium Chloride | 0.000 | 0.209 | Ca $Cl_2$ |
| **01-0338** | 17 | Hydrophilite, syn | 0.000 | 0.024 | Ca $Cl_2$ |
| **26-0918** | 16 | Halite, K-rich, syn | 0.000 | 0.168 | K0.2 Na0.8 Cl |
| **10-0348** | 39 | Calcium | 0.000 | 0.736 | Ca |

According to the chemical formula, the minerals contained in the MSAP are the chlorides of potassium, sodium and calcium. This is in conformity with the NAA analysis reported in Table 2 which highlighted that the quantitative value of sodium is 0.03 and calcium is 0.60% respectively. Therefore, it could be inferred that the minerals present in the MSAP sample are the mixtures of the chlorides of Na, K and Ca and possibly that of Mn., since the sample has 0.03%Na, 50.75%K, 0.60%Ca, 29.10%Cl, and 9.04%Mn, which proved that the MSAP is a combination of eutectic salts. Though, percentage of Na is very low, but due to its position on the periodic table and its higher reactivity, it cannot be easily displaced in a mixture.

## CONCLUSION

1. This research has shown the traditional process of production of MSAP and its analysis with potassium accounting for 50.75% as the major constituent in combination with chlorides and other elements in the mixture.
2. The XRD revealed that the MSAP has unique compositions of K, Na, Cl, and Ca, that formed the eutectic mixtures of Sylvite syn (KCl.Ca), Sodium Potassium Chloride (Na.K.Cl), Calcium Chloride ($CaCl_2$), and Hydrophilte, syn ($CaCl_2$), which can find uses in various areas of application amongst which include catalyst for synthetic rubber manufacturing, textile making, pharmaceutical uses, Aluminium recycling and heat treatment of steels.

3. Therefore, generation of MSAP as a useful potassium salt from maize plant wastes will reduce thermal combustion of waste plants on the farm land, assists in waste management disposal system, provides environmental cleanliness, reduce potash mining, and increase farm land by reducing flooding.

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