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Towards Arresting the Harmful Effect of Cyanogenic Potential of Cassava to Man in the Environment

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ABSTRACT

The cyanogenic potential of cassava, Manihot esculanta crantz and its environmental effect were investigated. The cyanide was extracted via cold dilute orthophosphoric acid extraction. The extract was hydrolysed using sulphuric acid for break down of linamarin to yield cyanide and the yielded cyanide was quantified using silver nitrate, ammonium hydroxide and potassium iodide as the indicator. Two varieties of cassava of high cyanogenic potential were studied. Cyanogenic potential of 399.36mgHCN/Kg fresh cassava tuber (IITA Black) and 1322.88mgHCN/Kg fresh cassava tuber (local variety) were obtained while 936.00mgHCN/Kg (IITA Black) and 719.68mgHCN/Kg (local variety) were obtained from the leaves. The environmental effect of these cyanogenic concentration based on lethal dose of 60mg/70kg weight adult was made, and it showed that with 45million tons of cassava produced in Nigeria within 2008 would be catastrophic to the entire universe but harnessing this cyanogenic potential would bring about environmentally friendly cassava processing.

KEYWORDS: *cassava, cyanogenic potential, linamarin, hydrolysis*

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I. INTRODUCTION

Cassava (*Manihot esculentus*) is a staple food of nearly one billion people in Africa, South America, Asia and the Pacific [1]. By its nature, cassava processing for starch extraction produces large amounts of effluent high in organic content, suspended solids, visible dust waste and hydrocyanic acid [1]. It is a major source of carbohydrate and it is the third largest source of carbohydrate in the world with Africa being the largest centre of production [2]. Nigeria is the largest producer of cassava in the world and cassava is also the major food crop in Nigeria [3]. About 45million metric tonnes of cassava was produced in Nigeria in 2008 and Nigeria's cassava transformation is the most advanced in Africa [4, 2]. Hydrocyanic acid (HCN) is toxic to man and hence much of the processing of cassava tubers is to remove HCN before to consumption. Fermentation is one of the means of removing HCN. In West Africa the principal form in which cassava is eaten is as a fermented meal known as Garri [2],

Lafun, Kpupuru**.** Of these different forms in which cassava is consumed, the tubers must be processed thoroughly to remove cyanide. There are two varieties of cassava; sweet and bitter varieties classified thus based on cyanogenic content [5]. The sweet cassava has very low cyanide content and the fresh tuber could be eaten fresh or raw while the bitter type must be thoroughly processed before consumption. The cyanide in cassava exists in the form of cyanogenic glycosides which upon hydrolysis liberate hydrogen cyanide which is poisonous to man and domestic animals with the lethal dose of 60mg to a 70kg man [6]. Cyanogenic glucosides and their catabolic enzymes in cassava are located in separate parts of the cassava tuber. The enzyme linamarase is situated in the cell wall, grating or injuring the tuber brings linamarase and linamarin in contact and hence degradation of linamarin to yield cyanohydrin which spontaneously degenerates to yield HCN at about pH 5 or through the enzyme hydroxynitrile lyase. The cyanohydrin is degraded to yield HCN [7, 5, 6, 8] as shown in fig 1.

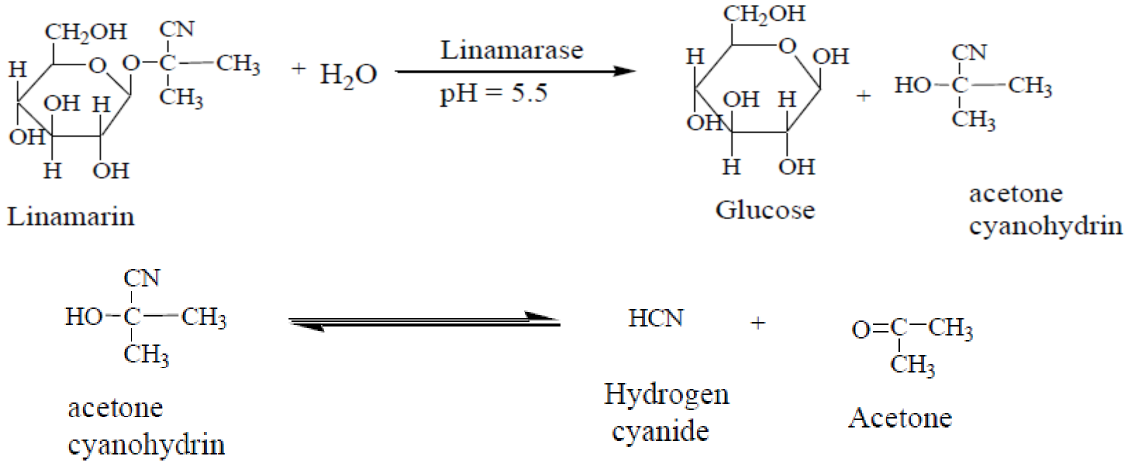

Figure 1: Hydrolysis of Linamarin [9, 10]

The hydrocyanic acid (HCN) is lethal if more than 100mg of it is contained in the food eaten by an individual at any one time [11]. If peeled tuber contain less that 50mgHCN/kg of the freshly grated cassava, the cassava can be taken as harmless to the consumer. A concentration of between 50mg and 80mg may be slightly poisonous, 80mg to 100mg is toxic, while concentrations above 100mg/kg of grated cassava are fatal [12]. The lethal dose range for humans of hydrogen cyanide taken by mouth for 60kg adult is about 30–210mg of HCN [13]. Presence of cyanide above the safe level of 10mgHCN/Kg cassava flour may pose health risk to the consumers. Since linamarin is bitter, high-cyanide cassava roots containing more than 100ppm cyanide are normally bitter and are called bitter cassava. One such variety in Nigeria is called ‘chop and die’. It is difficult to understand how cassava can be promoted without giving proper consideration to the fact that it contains a cyanogen (linamarin) that liberates poisonous cyanide in the body. [14]It was reported that in Amazonia and in Africa different varieties have a range of total cyanide contents in the parenchyma tissue from very low to very high (1–1550ppm). [14, 15] In other studies a concentration of 900–2000mg HCN kg^{-1} fresh weight was reported. The leaves in this study contained a second enzyme called hydroxynitrile lyase, which catalyses the hydrolysis of acetone cyanohydrin to produce HCN and acetone [2]. [16]Also a cyanogenic potential range of 100 – 900mgHCN/kg fresh cassava has been reported. Again, cyanogenic level of between 197.30 – 951.00mgHCN/kg fresh cassava has been reported[2]. High cyanogenic content of between 627.00mgHCN – 707mgHCN/kg has been reported also in cassava peels [

17]. When linamarin is hydrolysed, it releases cyanide (CN^-), a volatile poison. Cyanide is a potent cytotoxic agent that kills cells by inhibiting cytochrome oxidase of the mitochondrial electron transport chain [18]. However, some cyanide can be detoxified by the human body [2]**.** When ingested, cyanide activates the body own mechanisms of detoxification, resulting in the transformation of cyanide to thiocyanate, a compound that is less toxic [12, 19, 20, 18] and found in the serum, urine, sweat, saliva and tears of man and lower animals [18]. At the same time, it has been known as the precursor of HCN and supplier of the cyanide ion for the nitrilization of the precursor of vitamin B-12 (hydroxocobalamin) to vitamin B -12 (cyanocobalamin) [21]. This also indicates that HCN is a substance with fundamental physiological significance in man. The principal detoxification pathway of cyanide is that catalysed by a liver mitochondrial enzyme, ‘rhodanase’ (sulphur transferase). It is widely distributed in both plants and animals species [18]. The major function of the rhodanase is cyanide detoxification which is highly specific in action. It is limited not merely to nitriles but only to those nitriloside which surrender free HCN ions upon hydrolysis of linamarin [20]. However, development of thiocyanate in the presence of severe iodine deficiency has apparently been associated with goitrogenic effect in both human and animal populations. There has never been anything to suggest the possibility of any cumulative toxicity arising from the cyanide ion itself [20]. The nitriloside CN ion has been reported as a booster, raising both the red cell count and the total haemoglobin in animals and humans when small quantities of cyanides or various quantities of the nitriloside is given [20].Since the utilization of cassava roots for both human and animal nutrition is limited by the presence of cyanogenic glycoside, there is need for adequate processing to effectively remove cyanide from cassava products which must be looked into and employed during processing of cassava to edible products. This work aims at harnessing the cyanogenic potential of cassava for industrial application without releasing the cyanide into the environment to become an health hazard and the edible products for consumption.

Some of the health conditions associated with cassava meals includes Tropical Ataxic Neuropathy (TAN), Konzo – a spastic paraparesis of the leg attributable by consumption of insufficiently processed cassava [21]. In regions where there is iodine deficiency, consumption of insufficiently processed cassava part causes goitre and cretinism, cyanide intake from cassava exacerbates these conditions [2]. Consumption of cassava and cassava products containing large amounts of cyanide can cause acute intoxication, with symptoms of dizziness, headache, nausea, vomiting, stomach pains, diarrhoea and sometimes death. Since the lethal dose of cyanide is proportional to body weight [13, 2] children tend to be more susceptible to outright poisoning than adults [2]. The linamarin content of cassava flour was reported to be more than double during drought [14, 2], which leads to outbreaks of konzo; most recently there were more than 100 cases in Nampula and Zambezia Provinces due to drought in 2005 [2].

Some applications of cyanide include;

(1) Electroplating and surface treatment [22, 23].

(2) Sodium cyanide is used in extraction of gold and silver from the Ores and in metallurgy. It is also used as a reducing, dehalogenating, polymerizing, decolorizing, dehydrating, or condensing agent in many organic reactions [24, 25].

(3) It may be added directly to alkenes, for example, butadiene gives adiponitrile, $NC(CH_2)$ for nylon in the presence of Zero-valent Nialkyl phosphite catalyst [24].

II. METHODOLOGY

The two different varieties of cassava with high cyanogenic content used for cyanide extraction were the IITA black and local variety. Fresh cassava tubers and leaves were obtained. The tubers were washed and extracted with cold dilute orthophosphoric acid (0.1M) and the leaves were dried overnight in a drying cabinet at 60 to 70^{o}c and also extracted with cold dilute orthophosphoric acid (0.1M) and hydrolysed in a boiling tube with sulphuric acid (4M) in a boiling bath for 55 minutes and sodium hydroxide was added and allowed for the breakdown of cyanohydrin to yield HCN [26]. The cyanogenic potential (CNP) was quantified using the Deniges modified method [27] with Silver nitrate, ammonium hydroxide and potassium iodide as the indicator with the lethal effect of HCN on human population estimated.

III. RESULTS AND DISCUSSION

3.1 Results

Table 1: Cyanogenic potential of cassava tubers and leaves

CASSAVA VARIETY	CNP(mgHCN/kg fresh cassava	$CNP_T + CNP_L$
IITA black		
Tubers	399.36	1335.36
Leaves	936.00	
Local variety		
Tubers	1322.88	2042.56
Leaves	719.68	

NOTE: CNP_T – cyanogenic potential of cassava tuber
CNP_L – cyanogenic potential of cassava leaves
CNP values are averages of six (6) replicates.

Table 2: Estimated indoor lethal effect of HCN on Nigerians

mgHCN/kg fresh cassava	Estimated HCN that would potentially have been released to the environment (tons)	Number of people that would have been affected by CN^- (1 ton) released
Assumed		
100	4.5	355,555
Experimental values		
399.36	17.9712	1,419,946
719.68	32.3856	2,558,862
936.00	42.12	3,328,000
1322.88	59.5296	4,703,573

NOTE: Estimate, based on FAO cassava production value of 45 million tons of cassava roots by Nigeria in 2008[13, 3]

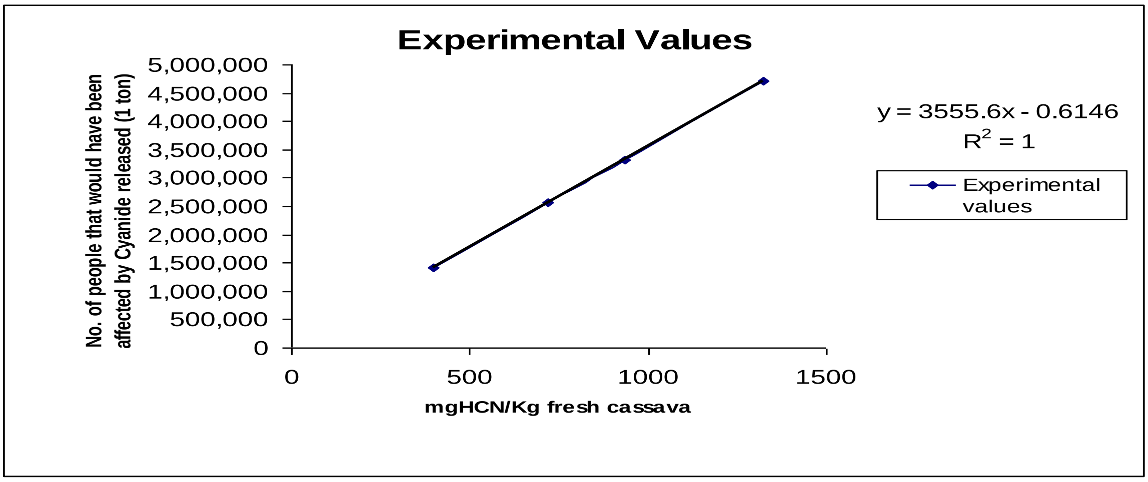

Figure 2: Graph of number of people that would have been affected by cyanide released (in tons) as against mgHCN/kg fresh Cassava

3.2 Discussion

The result presented in TABLE 1 showed IITA black with CNP of 399.36mgHCN/kg fresh cassava for tubers and 936.00mg HCN/kg fresh cassava leaves while the local variety has 1322.88mgHCN/kg fresh cassava tubers and 719.18mgHCN/kg for fresh leaves. This alone gives enough possibility of harnessing the total cyanogenic potential of cassava for application in industrial processes like case hardening of mild steel, extraction of gold and silver from their ores, some organic reactions and electroplating. Combining CNP obtained for tubers and leaves of the IITA variety we have 1335.36mgHCN/kg cassava while for the local variety we have 2042.5mgHCN/kg. This indeed shows that cassava can be a very readily available source of cyanide. This also signifies that environmental pollution of HCN through cassava processing effluent if not well harnessed can lead to severe health hazard to mankind.Let's attempt to estimate the effect of cyanide discharged into the environment through cassava processing. If we assume a modest concentration of 100mgHCN/kg fresh cassava for that year's production, then 4.5 tons of cyanide would potentially be released to the environment which would be fatal to 355,555 people. The relationship between number of people that would have been affected by cyanide released (in tons) and mgHCN/kg fresh Cassava was fitted into the linear regression equation:

$$y = mx + c$$

Fig 2 shows that the more the release of mgHCN/kg of Cassava, the more the increase in populace that will be affected or exposed to the harmful effect of cyanide. The slope of the regression equation for figure 2 ($m \approx 3555.6$) is positive and significant. The slope of the regression equation for the effect of cyanide released on the number of people was positive and greater than unity. The intercept is negligible. Whereas the squared correlation coefficients ($R^2 = 1$) of the linear model is significant implying that the exposure of people to cyanide is feasible.

IV. CONCLUSION

This work showed that cassava is a readily available source of cyanide. And also that harnessing the cyanogenic content of cassava for industrial application will help in creating a safe environment for cassava processors and maintain a safe environment.

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