

## Production of Sodium Cyanide from Cassava Wastes

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### ABSTRACT

An acid hydrolysis method of cyanide release from cyanogenic glucosides in cassava was investigated for the release of cyanide ion (CN<sup>-</sup>) to be used for the production of sodium cyanide from cassava. The released cyanide was fixed in Sodium Hydroxide after hydrolysis. Sodium cyanide was crystallized from the slurry by maintaining the temperature between 60<sup>o</sup>C and 70<sup>o</sup>C in a drying oven. Characterization of NaCN was done via the Deniges' modified silver nitrate titration. Cyanide concentrations between 140mg CN/50g to 342mgCN/50g of sample were obtained. The yield range was 0.28% - 0.68%.

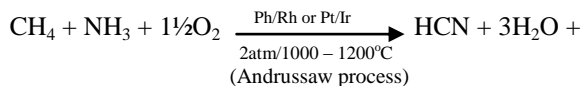
**Keywords:** Cyanogenic glucosides, Acid hydrolysis, Sodium cyanide

### I. INTRODUCTION

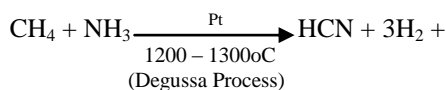
Cyanides, generally extremely toxic, contain the carbon – nitrogen triple bond (-C≡N), they are called cyanogen compounds depicting their ability to form deep-blue pigments [1]. Hydrogen cyanide (HCN), a colourless gas with a relative molecular mass of 27.03 g mol<sup>-1</sup> is a covalent molecule capable of dissociation in aqueous solution. This gas is evolved when cyanides are treated with acids.

In metallic cyanides, (e.g. sodium cyanide, NaCN), which are salts of hydrogen cyanide, the group -C≡N is present as the negatively charged ion CN<sup>-</sup>. At normal temperature, the CN<sup>-</sup> ion is rotationally disordered and is thus effectively spherical with a radius of 1.92Å hence, NaCN has the NaCl structure.

Hydrogen cyanide which was first isolated by Steele and Bertholet between 1782-3 is industrially prepared from methane (CH<sub>4</sub>) and ammonia (NH<sub>3</sub>) [1, 2]. This can be accomplished by one of the two routes indicated in equations 1 and 2.



144KCalmol<sup>-1</sup> ----- Eqn. 1



144KCalmol<sup>-1</sup> ----- Eqn. 2

After HCN is obtained it is converted to an alkali salt using a base [3]. This process comprises contacting sodium hydroxide with hydrogen cyanide. This contact brings about an ion

exchange where the -OH<sup>-</sup> is exchanged with the -CN<sup>-</sup> and sodium cyanide crystallized from the aqueous solution by evaporation at about 72<sup>o</sup>C – 75<sup>o</sup>C for about 13hours in a drying oven [4].

### II. CYANIDE COMPOSITION IN THE CASSAVA (Manihot esculenta crantz) TUBER

The cassava tuber flesh is composed of 60 – 70.25% water, 35% carbohydrate, 7 – 12% protein, trace amounts of fibre, about 1 – 2% mineral water. Most of the carbohydrate fraction is starch, which makes up 20 – 25% of the tuber flesh. Among the minerals in the tuber, phosphorus and iron predominate with minimal amounts of calcium. The tuber is relatively rich in vitamin C (35 mg per 100 g fresh weight) and contains traces of Niacin and vitamins A, B, and B<sub>2</sub> but the amounts of thiamine and riboflavin are negligible [5, 6]. Cassava tuber contains small but significant amounts of the cyanogenic glucosides, linamarin and lotaustralin in the ratio 93:7. Linamarin is manufactured in the leaves and translocated as the diglucoside Linustatin to and stored in the roots [7, 8, 9].

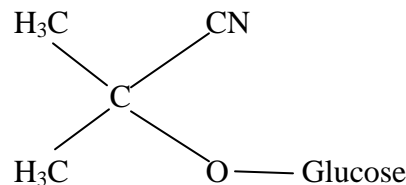


Figure 1: Structure of Linamarin

Cassava cultivars have been classified into two; bitter and sweet cassavas on the basis of cyanogenic content. The bitter variety has the cyanogenic glucoside distributed throughout the tuber at

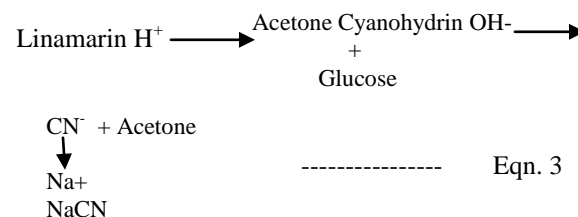
a high concentration and the sweet variety has the cyanogenic glucoside confined mainly to the peel and is at low concentration [5].

Nigeria was quoted by the Food and Agriculture Organization (FAO) to have produced 26million tons of cassava roots in 1989/90. Driven by this figure an earlier study by AttahDaniel and co-researchers [18], showed that if 100mg CN was discharged into the environment, 2,600 metric tons of cyanide would have been discharged into the environment. We believe it is worth while therefore to attempt producing metallic cyanide from cyanide released from cassava.

The small but significant concentration of cyanogenic glucosides makes utilization of cassava for nutritional purposes in humans and animals limited. The hydrolysis of the Cyanogenic glucosides, which could be achieved by bringing the enzyme linamarase in contact with the cyanogenic glucoside or via acid hydrolysis, yields hydrogen cyanide [10]. Rosling [11] reported cyanogenic glucoside concentration of 1500 mg HCN equivalent Kg<sup>-1</sup> dry weight in fresh roots of bitter cassava. Okafor [12] also reported that more of the cyanogens are concentrated in the peel of the sweet cultivar and about 200 mg HCN Kg<sup>-1</sup> are present in the leaves. Cyanogenic range of between 197.3 – 951.5 mg HCN Kg<sup>-1</sup> has also been reported by Agbor-Egbe and associates [13].

The method of acid hydrolysis of linamarin was developed via NMR experiments [14]. Its simplicity and cost effectiveness makes it a preferred method of cyanide release in this work. The released cyanide ion is hereafter fixed in sodium hydroxide to yield sodium cyanide via an exchange of the -OH negative

ion in sodium hydroxide with the released CN<sup>-</sup> from the hydrolysis process as shown in equation 3.



### III. METHODOLOGY

Cassava samples were treated with cold 0.01000M ortho phosphoric acid to extract the cyanogenic glucoside. The extract was hydrolyzed to the corresponding Cyanohydrin using 4M Sulphuric acid in a stoppered boiling tube at 100°C for fifty-five (55) minutes. Cold dilute ortho phosphoric acid was used because of the high volatility of cyanide (about 1.1 x10<sup>6</sup>mg/m<sup>3</sup> at 25°C). This was followed by spontaneous disintegration of Cyanohydrin to release CN<sup>-</sup> which was fixed in 3.6M sodium Hydroxide to yield Sodium Hydroxide [15, 16].

The Sodium cyanide in aqueous solution was crystallized by maintaining the temperature between 60°C and 70°C for about 13hours in a drying oven. The Sodium cyanide crystals were quantified using Denige's modified Silver Nitrate titration method of cyanide.

### IV. RESULTS AND DISCUSSION:

**Table 1: Concentration Of Cn<sup>-</sup> In Mg/HCN And Quantity Of NaCN Obtained**

Cassava Sample	Fresh leaves	Fresh peels	Fresh tuber tissue	Fresh whole tuber tissue	Dried leaves	Dried peels	Dried whole tuber
mgCN in 50g sample	300±6	268±9.2	342±2.6	266±3.2	160±3.2	140±1.0	232±4.2
% yield CN <sup>-</sup>	0.60	0.54	0.68	0.53	0.32	0.28	0.46
Weight of NaCN salt (g)	2.84	2.75	2.94	2.64	2.31	2.14	2.56
% yield of NaCN (%)	5.68	5.50	5.90	5.27	4.61	4.27	5.11

Sodium cyanide usually produced through the Andrussaw process or the Degussa process reacting methane and ammonia in the presence of a catalyst to yield HCN, after which the HCN is contacted with Sodium Hydroxide to yield NaCN can be prepared by a much shorter route using CN<sup>-</sup> released from the hydrolysis of cyanogenic glucosides from cassava.

This work we believe can be a simplified and shorter route to producing cyanides. We took into consideration the fact that Sodium Cyanide has the ability to dissociate in aqueous solution and has the Sodium Chloride structure [1] in the

crystallization of the Sodium Cyanide from the slurry after fixing the released CN<sup>-</sup> in Sodium Hydroxide.

The results in Table 1 show that 2.84g of NaCN was obtained from fresh leaves sample which is about 5.68% of the total weight of sample while the fresh peels had 2.75g NaCN/ 50g sample, also about 5.50% of the sample weight. 2.94g NaCN, 2.64g NaCN, 2.31g NaCN, 2.14g NaCN and 2.56g NaCN were obtained for samples of fresh tuber tissue, fresh whole tuber tissue, dried leaves, dried peels and dried whole tuber respectively and their respective percentage yields were; 5.90%, 5.27%, 4.61%, 4.27% and 5.11%.

The percentage cyanide for the samples of fresh leaves, fresh peels, Fresh tuber tissue, fresh whole tuber tissue, dried leaves, dried peels and dried whole tuber obtained were 0.6%, 0.54%, 0.68%, 0.53%, 0.32%, 0.28% and 0.46% respectively.

## V. CONCLUSION

This work showed the possibility of producing cyanides from cassava by yet another route different from the Andrussaw or the Degussa process the Andrussaw method of producing cyanides.

Cyanide production from this process is simplified and cost effective. The method does not require complicated equipment, huge energy supply to attain high temperature of between 1000 to 1300<sup>0</sup>C and use of Catalyst as is the case with the Andrussaw or Degussa methods which involve production of Hydrogen cyanide from methane and ammonia and later contacting the hydrogen cyanide with sodium hydroxide to give sodium cyanide.

We can also conclude that it opens up a way for producing cyanides cassava processing.

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