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# Environmental Contamination from Industrial Bitter Cassava: Implications for Moisture-Pressure Combination Treatments

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**Abstract**

Commercial processing of cassava produces vast quantities of cyanide-laced waste which can adversely infiltrate water supplies and air breathed by factory workers. This study aimed to determine the comparative concentration of cyanogens in the cassava peel as opposed to that of the pith and the effect of the moisture-pressure combination treatments on cyanide concentration. A semi-quantitiative test using the picrate-spectrophotometer method was applied, where, at room temperature in a closed vial, reactions caused liberation of HCN which reacts with a picrate paper. The results showed a 25% higher level of cyanogen concentration in casssava peels compared to that of blended peels and pith. Treatments released cyanide from samples in the order: 2 h wetting at 50 °C + pressing > 4 h wetting at 25 °C + pressing = 2 h wetting at 40 °C + pressing > 2 h wet at 25 °C + pressing = 4h wet at 25 °C > 12 h pressing. In this manner, wetting for 2 h at 50 °C followed by pressure for 12 h released cyanide by at least 20% more than that of any other treatment. The combination of moisture and pressure enhanced the contact time between linamarin and linamarase to increase the release of HCN. Physiological cyanide overload in organisms from cassava processing occurs in water, land, and air. Therefore the reduction in concentration observed in this study, if applied at an early stage of the cassava processing, should reduce the rate of morbidity in environments at risk.

**Keywords:** cassava beer, cassava cyanide, cyanogen, linamarin, gari

## 1. Introduction

Starch finds uses in fast food, sweets, sausages, tablets, paper, corrugated board etc. and plays a prominent part in everyday life (International Starch Institute, 2014) including, in recent years, beer-manufacturing in parts of Africa, followed by Jamaica. However, the many varieties of cassava fall into two main categories, namely bitter and sweet cassava (respectively, *Manihot palmata* and *Manihot aipi*) (International Starch Institute, 2014), depending on their content of cyanohydrin. For industrial purposes bitter varieties are most often used because of their higher starch content (CAADP, 2010; International Starch Institute, 2014), being better suited to the production of high-value starch and maltose for industrial use (CAADP, 2010). Farmers, like commercial operators, often prefer the bitter (most dangerous) varieties because they deter pests, animals, and thieves (Oluwole et al., 2014). Sweet cassava is preferred for food due to its taste and dough forming facility (Juang, 2001).

Cassava wastewater contains toxic materials that can endanger humans, as well as other living organisms if they are not properly treated before disposal (Okafor & Maduagwu, 2000). Cyanogenic concentrations in cassava roots range from 10-500 mg HCN (Siritunga & Sayre, 2004), up to fifty times greater than the recommended safe levels of 10 ppm for human consumable food products (FAO/WHO, 1991) and levels exceeding 100 ppm are a health danger (Bokanga, 1994; Ernesto et al., 2002; Manjunatha et al., 2015; Minerals Council of Australia, 2016). During cassava starch production, large amounts of cyanoglycosides are often released and hydrolyzed by plant-borne enzymes, leading to cyanide concentrations in wastewater as high as 200 mg $L^{-1}$ (Siller & Winter, 1998). Akinrele (1986) reported that large scale cassava processing could be hazardous, not by consuming residual cyanide in food, but the discharge of hydrocyanic acid into the air. In this context, the hydrocyanic acid contamination of the atmospheric air (Okafor & Maduagwu, 2000) and natural water sources (Okafor et al., 2001; Otuu et al., 2014) in areas near large scale "gari" processing as well as possible occupational exposures of humans to cyanide poisoning during large scale cassava processing (Okafor et al., 2002) have been reported.

They found a statistically significant difference ($p$ value < 0.05) between the mean thiocyanate excretion of the processors and the consumers, such that gari processing is the highest source of cyanide exposure among Nigerian communities dependent on cassava as their major staple. Hydrogen cyanide was readily absorbed from the skin or inhaled during roasting of gari, and converted to SCN in the liver and kidneys (Okafor et al., 2001).

*1.1 Usefulness of Thiocyanate as a Marker*

Urine thiocyanate SCN is a useful biomarker of exposure to cyanide from cassava foods (Okoh, 1983; Oluwole & Oludiran, 2014), and there is strong ecological association of exposure to cyanide and endemicity of ataxic polyneuropathy (Oluwole & Oludiran, 2014). The $HCN^-$ ion is readily absorbed by the gastrointestinal tract and is rapidly converted into thiocyanate by the enzyme rhodanese (WHO, 1996). Oral and subcutaneous doses of cyanide in rats are excreted as thiocyanate, primarily in the urine (Okoh & Pitt, 1982; Okoh, 1983). Plasma proteins (especially albumin) are known to be involved in cyanide detoxification via its conversion to thiocyanate (Manahan, 2009). Nevertheless, the amounts of sulphur needed to detoxify ingested cyanide of cassava is very small compared with the daily intake of sulphur containing amino acids and therefore cannot affect levels of protein energy malnutrition (Bradbury & Denton, 2010). In other words, physiological detoxification of cyanide does not cause protein deficiency. The corollary is that even an adequate level of dietary protein cannot confer protection against the effects of exceeding maximum limits.

*1.2 Commercial/Industrial Advantages of Cassava*

In the tropics, large-scale cassava inputs for beer-making and soft drinks are a commercially less costly alternative to the importation of barley malt and corn syrup, based on the following reasons:

- It is affordable not only as a nutrition source but as a commercial and industrial source of starch.
- Cassava is one of the most drought-tolerant crops, growing successfully in marginal soils.
- Yields are reasonable where many other crops do not grow well.
- Cassava is well adapted within latitudes 30° north and south of the equator, at altitudes up to 2,000 m (6,600 ft) above sea level in widely ranging rainfall regimes, and to poor soils with a pH ranging from acidic to alkaline.

The USDA Foreign Agricultural Service (2014) reports the following:

China is poised for a 6% increase in the manufacture of biofuels. The government is encouraging development of non-food grain feed stocks, such as cassava and sweet sorghum.

However, these crops still compete with food crops for land, and only one cassava and one sweet sorghum ethanol plant are approved for production by the government. Currently 8% of fuel ethanol is produced using cassava.

The 11th Five-Year Plan (2006-2010) set goals for expanding non-grain based ethanol production, targeting cassava and sweet sorghum. The world's first cassava ethanol plant was built in Guangxi in 2007 with an annual production capacity of 200,000 tons.

Dai et al. (2006) claim that cassava fuel ethanol is more energy efficient than gasoline, diesel fuel and corn fuel ethanol but less efficient than biodiesel (Dai et al., 2006). However, with reference to gasoline, the opposite position is stated by the USEPA (Dunham, 2006). Through fuel ethanol production, one Joule of petroleum fuel, plus other forms of energy inputs such as coal, can produce 9.8 J of fuel ethanol (Dai et al., 2006). Biodiesel from cassava was expected to be to 200 thousand tonnes in 2010. This is equivalent to 10 million tonnes of petroleum. Cassava starch production therefore, is potentially a growing activity in the tropics.

*1.3 Study Area*

1.3.1 St. Thomas-Kingston Sub-Region

Cassava plantations in the southeast section of Jamaica for supplying a beer brewery in the same sub-region have been established. Being a rain shadow zone (Figure 1), calm conditions often prevail.

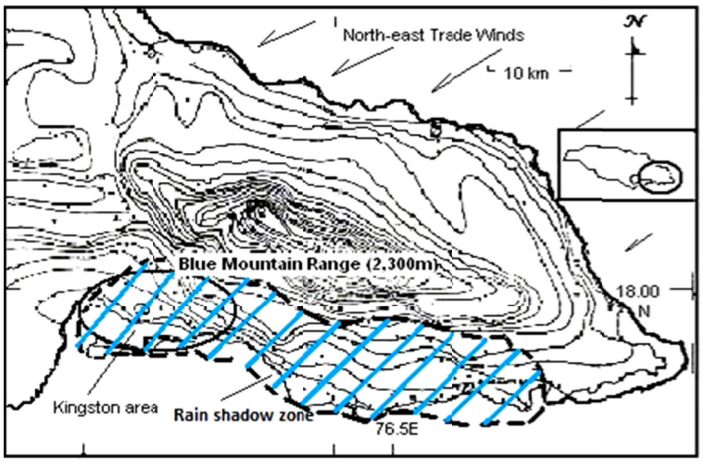


Figure 1. The location of cassava-processing in southeastern Jamaica

*Note*. The beer brewery is located south of the Blue Mountain Range in the rain shadow zone.

Diurnal temperatures range from 20-35 °C (April-September) and 17-35 °C (October-March) with average monthly temperatures varing by 2.5 °C. The annual average temperature is 27.1 °C. There is no cold season.

Kingston's climate can be classified as a tropical wet and dry/savanna climate (Köppen-Geiger classification: Aw) with a pronounced dry season in the months having a low-sun-altitude (December-April) months. The wet season occurs in months dominated by a high sun-angle (June-November). Total annual precipitation averages 811 mm. On the other hand, north-eastern Jamaica receives more than three times as much rain mainly from the North-east Trade Winds (Figure 1).

*1.4 Dangers of Cassava Processing in Study Area*

In Jamaica, referring to the "cassava starch in beer" project, Kareena (2014) stated: "Once the cassavas reach the factory, they will be placed on a scale and placed in silos. From there, water and a mechanical agitator are used to start processing the cassava. The roots will then go through a rasping (grating) after which a wet extraction will be done. This process involves the repeated washing of cassavas and putting them through a series of hydro sieves where the starch precipitates out of the product. The product is then continuously dried using a sieve and cyclone and then scraped and placed in a fluidized bed drier, which is a hot stream of dry air to dry the wet starch to a starch powder. The powder will then be used in the production of beer." Therefore, from the above account of the production process, it is unclear as to whether the rind (this is not merely outer skin) of roots will be discarded or used to increase the starch quantities.

The "land and sea breezes" in the study area (Figure 1) are weak, compared with those of the Trade Wind system of the northern section of the island. Such mainly calm conditions and insufficient air movements (Figure 2) should fail to efficiently dilute and disperse toxic atmospheric gases. Otuu et al. (2013) refer to the clustering location of cassava processing plants without any designated site for waste disposal. To improve public health of the inhabitants, their study was expected to guide relevant government agencies on relocation of existing cassava plants to minimize effluent infiltration into wells. In this context, buildings without adequate designated sites for disposal of cassava solid peels and liquid wastes remain a health concern.

Otuu et al. (2013) note that the location with regards to slope influences cyanide content to a greater degree than the linear distance. Thus two sites at varying distances from the processing plant had the same cyanide content because the closer site was located on a slope, which enhanced the flow of the effluent into the well water.

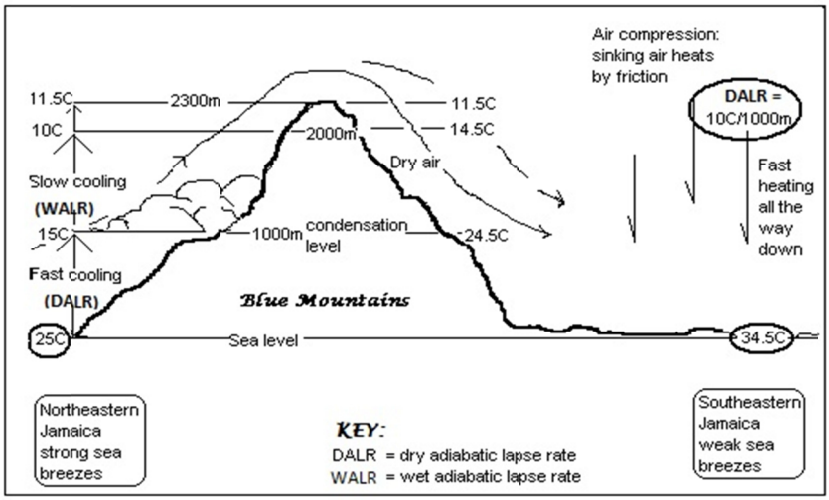


Figure 2. Calm atmospheric conditions of southeastern Jamaica are inimical to the dilution and dispersion of environmentally toxic gases

*Note*. Drawn by M. A. Harris.

*1.5 Previous Processing Methods*

Very little research except Bolhuis (1953) has been published on the effectiveness of the pressing method for releasing HCN from freshly grated cassava root. However, Bradbury and Denton (2010), and Cumbana et al. (2007) found that wetting fresh shredded cassava with added linamarase in water for 5 h decreased cyanide levels by up to 84% in 5 g samples. Nevertheless, as many cassavas contain low levels of linamarase (Bokanga, 1994), such favourable results were often obtained when the enzyme linamarase was deliberately added to the sample (Bradbury & Denton, 2010), and the cost of such enzymes is often prohibitive. Further, the wetting treatment would be insufficient for cassavas containing > 300 ppm of cyanide because > 50 ppm cyanide (a safety limit) would remain in the product. Therefore Harris and Koomson (2011) studied the effects of moisture-pressure combination treatments on the removal of cyanide from bitter cassava. They found that pressure for a specified time, when prededed by moisture applications, decreased the concentration of cyanogens as compared with any wetting treatments. Harris and Koomson (2011) reported that traditional 12 h pressing of grated bland or bitter cassava roots containing sufficient reactants rarely reduced cyanide concentration to safe levels. They discovered that although long wetting was more efficient at releasing HCN than pressing, pressing following wetting was more efficient at releasing HCN than either wetting or pressing acting alone. Thus, of all their treatments, pressing for 12 h was easily the least effective, but the combination of moisture and pressure increased contact between linamarin and linamarase to increase the release of HCN.

This research aims to study the differences in cyanogen concentration between peeled and unpeeled cassava roots and the effects of moisture-pressure combination treatments on the whole tuber inclusive of pith and peel.

Cyanogens in plants protect against destruction by predators seeking food (Minerals Council of Australia, 2016). Thus, it is supposed to hypothesize that highest levels of cyanogens are located in the outer section (peel, or, rind) of the the cassava tuber.

Moisture-pressure treatments are more effecient than moisture and/or heat in removing cyanogens from whole cassava tubers (pith + peel).

## 2. Materials and Methods

*2.1 Cassava Treatments*

Cassava tubers were thoroughly washed in de-ionized water, and dried. The gratings of peeled or unpeeled (rind + pith) bitter cassava roots were soaked overnight after Harris and Koomson (2011).

*2.2 Moisture-Pressure Treatments of Grated Cassava*

Both peeled and unpeeled, grated cassava, were subjected to soaking and pressure according to the method of Harris and Koomson (2011) as follows:

Some of the fresh, grated material was divided up and pressed for 12 h (P). For pressing, twenty grams of grated cassava were placed in an 8 × 12 cm cotton cloth bag and the bag placed on a concrete surface inclined at 30 degrees from the horizontal. A 30 × 15 × 10 cm concrete block weighing 10 kg was placed on the sample and left in that position for 12 h. The inclined surface was evaluated as a necessary step to facilitate the potential outward flow of liquid from the porous sample bag. All other samples were wet in the proportion 1:1.25 cassava: water (w/w) for 2 h at 50 °C. This is because Harris and Koomson (2011) found that wetting for 2 h at 50 °C removed more cyanogens than wetting at temperatures below 50 °C. This was followed by pressing (P) for 12 h.

For total cyanide content analysis, linamarase/buffer papers were placed in plastic vials. Samples of 100 mg were added followed by picrate paper and a lid. The vials were kept at room temperature for 18 hrs, the picrate paper was removed from the plastic strip and the paper eluted for 30 min with 5 mL of distilled water. The absorbance (A) of the solution was measured using 10 mm cuvettes in a Genesys 20 spectrophotometer in the direct reading mode, against a blank solution prepared from a 4 $cm^2$ picrate paper not exposed to HCN and eluted with 5 mL distilled water. The total cyanogen content in mg HCN equivalents/kg sample (ppm) was calculated by the equation (Bradbury et al., 1999):

$$ppm = (396 \times A \times 100)/z \quad (1)$$

Where, A = absorbence (nm), and z is the mass of the sample (mg).

*2.3 Statistical Method*

Three replicates were compiled for each treatment. Statistical analyses were conducted on treatment means using the parametric Student's t-test to test the difference between means of independent samples at a 5% level of significance.

## 3. Results and Discussion

*3.1 Cyanide in Peel vs Pith*

Table 1 depicts the concentration of cyanide in freshly grated peeled cassava or unpeeled cassava. It can be seen that concentration in peel + pith exceeded that of the pith by > 25%. For the t-test, this result was significant at ($p$ = < .05).

Table 1. Concentration of cyanide in peeled vs unpeeled + peeled cassava

| Samples | Replicates | Mean | S.D. |
|---|---|---|---|
| Pith + peel | 287, 263, 297 | 282.20 | 17.70 |
| Pith | 244, 221, 196 | 220.30 | 24.50 |

Hence, as the concentration in the peel had been diluted by that of pith, the difference between the two zones is even greater than that shown by the calculations. Such high increases by the cassava outer pith occurring on a large scale can lead to significantly increased contamination of factory air and waste water in the environment.

Nevertheless, as the samples in this case were within the same cassava variety, more studies may be required.

*3.2 Moisture-Pressure Treatments*

Table 1 shows the total levels of cyanide in samples after treatment of fresh grated cassava. In this study, the most effective treatment is pressing for 12 hours after wetting (without added linamarase) for 2 hours at 50 °C, which reduced cyanide in a bitter cassava from 284 ppm cyanide to 38 ppm, an 87.2% drop. The amount of cyanide remaining in samples after that treatment was therefore only 12.8%. But, using the same cassava varieties and applying moisture-pressure combination treatments, Harris and Koomson (2011) reduced similarly high cyanide concentration in the ambient surroundings. They observed the greatest reduction of cyanide from the 2W50 treatment in the following order: 2WP50 > 4WP25 = 2WP40 > 2WP25 > 4W25 > 2W25 > 12P. These results show that even more bitter cassavas could be brought down to much safer levels with this treatment. Therefore, even for cassava peels, the method of Harris and Koomson (2011) could reduce this high cyanide concentration in the ambient surroundings.

Also, these results, like those of Harris and Koomson (2011) again exceeded those of Bradbury and Denton (2010) who achieved a maximum of 16% of cyanide remaining in their samples when they applied wetting only for 2 hours at 50 °C.

Linamarin breakdown varies directly with the availability of linamarase, and the amount of linamarase lost through its catalysis of linamarin breakdown varies directly with temperature and duration of wetting. In this study, linamarase acted efficiently due to increased rupturing of cells. This was also observed by Harris & Koomson (2011), where the high viscosity amylopectin with molecules (up to 80,000,000 in mass with many branch points) mainly comprising the cassava gel (WHO, 1974) could have sealed off internal conduits, thereby trapping cyanide gas in internal pores of the gel mass of their treated samples.

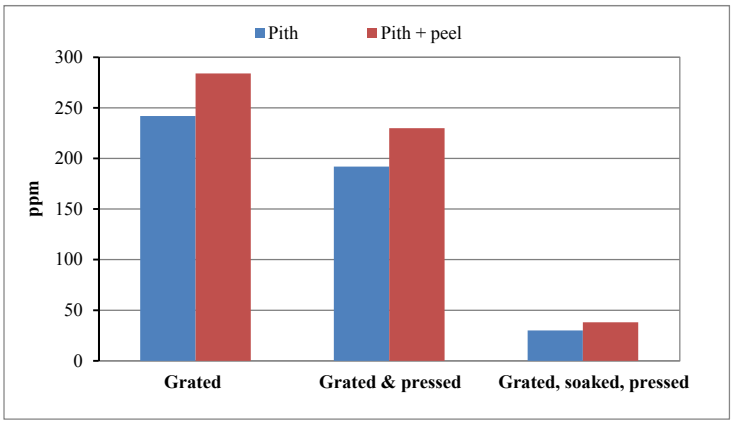


Figure 3. Cyanogen remaining in cassava tuber after treatment

As release of reactants for the production of HCN occurs only after the rupture of cells, this implies the rupturing of cells during pressing. A longer time-period of contact between enxyme and substrate combined with a higher concentration of reactants contributed to the increased release of HCN. However, though some rupturing must have occurred, there is no proof that rupturing is the only cause of the high level of cyanide release. On the assumption, therefore, that pressing merely expelled pre-trapped HCN gas from gelatinized samples, the effectiveness of the treatment is even more convincing.

## 4. Conclusions

Higher cyanide levels exist in cassava peels compared with the pith. Removing the peels before processing bitter cassava can reduce the concentration of cyanide in the atmosphere of factories which process bitter cassava. However, environmentally safer disposal of unwanted bitter cassava peels requires further research.

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