Review Article

WASTE-TO-WEALTH APPLICATIONS OF CASSAVA CYANIDE– A REVIEW STUDY OF INDUSTRIAL AND AGRICULTURAL APPLICATIONS

ABSTRACT

Cassava plant and its products have long been used as food and feed but lately as industrial ingredients. The present study unveils various agricultural and industrial applications of cassava especially the waste cyanogenic component which hitherto has constituted a huge agricultural waste. The study reviewed current engineering values which cassava cyanide has created in the industrial sector. Some very exciting ongoing research studies on engineering applications of the cassava cyanogenic glucoside are also highlighted.

Keywords: *cyanogenic glucoside* cassava, cyanide, pack-cyaniding, linamarin, waste

1.0 INTRODUCTION

Cassava originated in Brazil and Paraguay but was carried to Africa by Portuguese traders from the Americas. It is a perennial woody shrub, grown as an annual crop and serves as a major source of low cost carbohydrates for populations in the humid tropics (O'Hair, 1995). In the past, the largest producer of cassava was Brazil; followed by Thailand, Nigeria, Zaire and Indonesia (O'Hair, 1995) but today Nigeria is the largest producer (Oke, 2005).

The cultivation of cassava is basically simple. Cassava is a tropical root crop, requiring at least 8 months of warm weather to produce a crop. Cassava does not tolerate freezing conditions. It tolerates a wide range of soil pH 4.0 to 8.0 and is most productive in full sun (O'Hair, 1995).

Cassava has achieved considerable agricultural importance as the major source of tapioca and fodder for cattle, particularly in the European Economic Community (Nestel, 1973; Phillips,

1974). The utilization of cassava in human and animal nutrition is however, limited by the possibility of chronic and acute cyanide toxicity resulting from continuous consumption (Coursey, 1973).

Pack-cyaniding of mild steel using cassava leaves and the characterization of the case formed have been reported (Akinluwade, 2010; Adetunji *et al*., 2008; Ibironke *et al*., 2004). The presence of cyanogenic glucoside in cassava plant could be the accumulation of products of catabolism of amino acids (Conn, 1973) or a mechanism for deterring predators (Hosel, 1981).

Cassava has achieved considerable agricultural importance as a staple food for more than 500 million people, especially in the tropics (Egan *et al*., 1998). Previous investigation into this cyanide toxicity (Bradbury *et al*., 1999; Haque and Bradbury, 1999; Haque and Bradbury, 2002) was aimed at destroying the cyanide content in order to render cassava less harmful to the consuming populace. (Adetunji 1991)

Earlier work has investigated the industrial utilization of the cyanide product in cassava especially in the cyanidation of gold (Adetunji, 1991). Ibironke *et al*. (2004) have studied the case-depth measurement, with the utilization of mathematical modeling, for the pack cyaniding process using cassava leaves. Adetunji *et al*. (2008) reported metallographic studies of pack cyanided mild steel using cassava leaves.

Akinluwade *et al*. (2012) developed an environmentally friendly in-situ pack-cyaniding technique. The study concluded that pack-cyaniding was feasible with cassava leaves and has the potential to boost the economic viability of the plant for a developing economy. Akinluwade *et al*. (2013) studied visible diffusion zone of mild steel pack cyanided in processed cassava leaves using light and electron microscopes. He found that the visible diffusion zone is a region of high carbon concentration owing to diffusion of carbon from processed cassava powder and that the microstructure of the cases consists of a predominant pearlite phase while the cores are composed of predominant ferrite for high temperature pack

cyaniding. Ogundare (2014) undertook the production of gold nanoparticles from gold ore leached with cyanide sourced from cassava peels and leaves. Renee *et al*. (2013) investigated the influence of severe plastic deformation on tribological properties of mild steel samples case-hardened using processed cassava leaves.

2.0 REVIEW STUDY

Cassava tubers are traditionally processed by a wide range of methods, which reduce their toxicity, improve palatability and convert the perishable fresh root into stable products. The processing of cassava into its useful products is discussed in the following paragraphs.

2.1 Food and Feed

Garri is a creamy white, starchy, pre-cooked grit produced by fermentation of peeled, washed and mashed cassava roots which are dehydrated, sieved and roasted (Onyekwere, 1989), In Nigeria, over 70% of the cassava yield is processed into *garri* (Sanni and Olubamiwa, 2004). Its ability to store well and its acceptance as a convenience food are responsible for its popularity in West and Central Africa where it is a staple food.

The consumption of improperly processed cassava with high cyanogens content has been associated with cretinism, endemic goiter (Ermans *et al*., 1980; Delange *et al*., 1983) and even death. In addition to the toxic effect, the use of cassava roots as food is limited by their low protein content, short shelf life (Westby, 2002) and seasonal variability.

The traditional processing technique for *garri* production (Grace, 1997) has been modified to include: (a) addition of water to the freshly grated cassava at 75% (v/w) level, heating at 50°C for 6 h and equilibrating with a 3-day fermented cassava liquor (40% v/w) for 12-18 h, dewatering and toasting (Sokari, 1992), (b) the fresh tubers are peeled, washed, sliced and dried into chips which are then milled and fermented (Oguntimein, 1992), or rehydrated by

addition of water and fresh cassava mash (FIIRO, 2004) fermented, dehydrated and sieved before roasting to produce *garri*.

Cassava roots and cassava leaves are both used for animal feed (Buitrago, 1990, Dahniya, 1994). Cassava roots are rich in digestible carbohydrates, mainly in starch. Cassava starch granules are composed mainly of two polysaccharides, amylase (20%) and amylopectin (80%) (Sandoval, 2008). Therefore, cassava roots are low in protein and fat. Cassava root has less than the recommended minimum limit in almost all essential amino acids, except tryptophan (FAO, 1990). Cassava leaves are much richer in protein than the roots, although the leaf contains a lower proportion of methionine than the root protein. Cassava is good source of dietary fibre, magnesium, sodium, riboflavin, thiamine, nicotinic acid and citrate (Bradbury and Holloway, 1988). Cassava however contains cyanogenic glycosides linamarin and lotaustralin in a ratio of 97:7 in all its tissues except for the seeds (Teles, 1995). Cassava is usually classified by farmers as being bitter or sweet depending on the levels of anti-nutritional factors therein. Cassava varieties with bitter taste are considered toxic (Chiwona-Karltun *et al*., 2004).

In order to reduce toxicity and improve palatability of cassava, various treatment methods are being applied. Such methods include, peeling, boiling, steaming, shredding, roasting, fermentation, however the most common practices is drying of the roots after chipping (Garcia and Dale, 1999). The majority of farmers in Southern Africa prefer to grow the bitter varieties of cassava as a form of crop protection measure against pests. It is therefore imperative that cassava must me adequately processed or treated before it is used as an animal feed.

Processing cassava for animal feeds

This section discusses the processing of cassava into animal feed in the form of chips, pellets and feed grade single cell protein. The cassava plant, made up of the roots, leaves and stem,

is a good source of carbohydrate and protein. The different parts of the plant can be used as animal feed. The leaves can be used as silage, dried for feed supplementation and as leaf meal for feed concentrates. The stem can be mixed with leaves and used as ruminant feed, or dried for feed concentrates. The roots can be chipped or pelletized and used as feed, while the root peel, broken roots, fiber and baggase from starch extraction and garri processing can be dried and used directly as animal feed or as substrate for single cell protein production. The use of cassava root as animal feed is increasing in importance in the developing countries of Latin America and Asia where an export market for this commodity has developed.

Processing of cassava into chips and pellets

The flow chart for this process is shown in Figure 1. There is very little difference in the technologies used at different scales of chip and pellet production. The main difference is in sun-drying and mechanical drying. Chips can be produced by very simple techniques in the household or village as well as on a large mechanized scale.

About 2.5-3.0 tonnes of fresh roots are required for 1 tonne of pellets giving a conversion rate of 33-40 %. The first step can be washing and peeling, depending on the quality of the harvested roots.

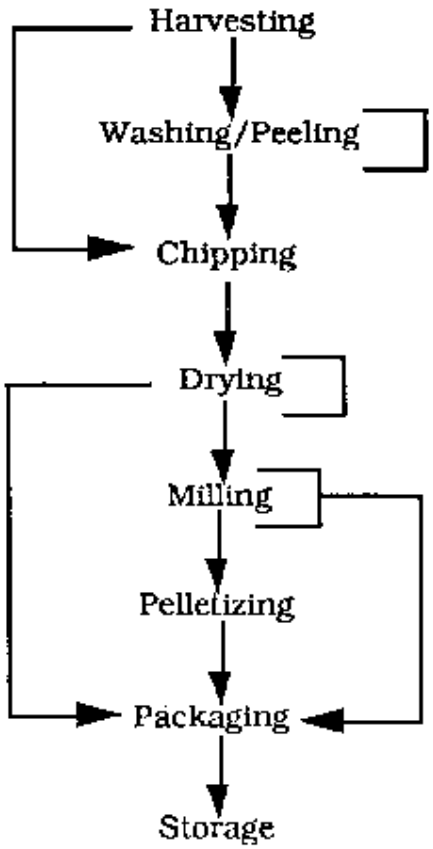

Figure 1: Flow chart for the production of cassava chips and pellets (Hahn *et al*., 1988)

Processing of cassava leaves and stems

Dried cassava leaves and stems can be fed to pigs, poultry, and dairy cattle. The meal produced from them has a nutritive value similar to that of alfalfa though deficient in methionine, isoleucine and threonine (Peyrot 1969, Rojanaridphiced 1977, Normanha 1962). Cassava leaves are a good source of about 20% protein. The amount of protein depends on the stage of growth. The processing of the aerial part of the cassava plant made up of both the leaves and the stem is shown in Figure 2. For the extraction of cassava leaf protein, the leaves and the stem are interacted in a chopper or grinder and the juice pressed out.

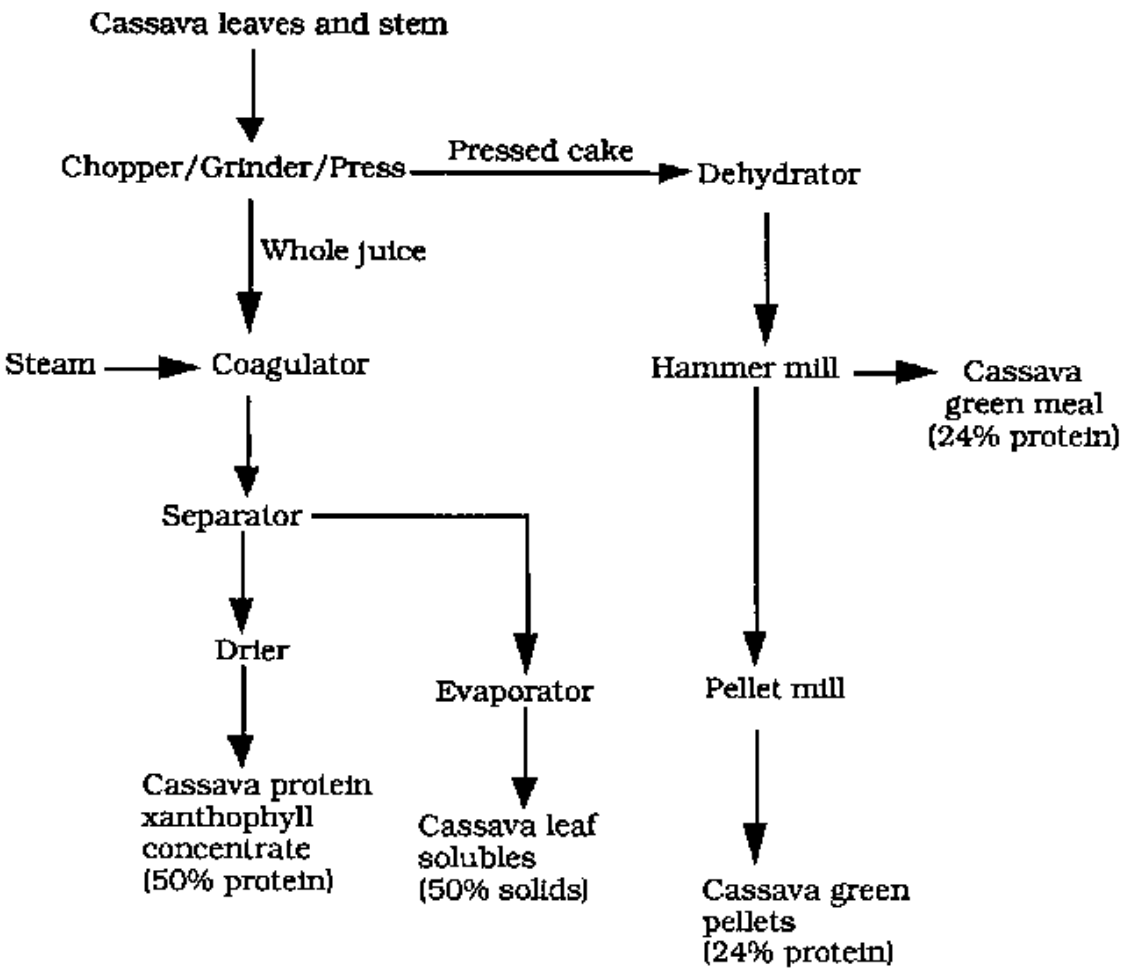

Figure 2: Flow chart for processing cassava leaves and stems (Hahn *et al*., 1988)

The extracted juice is then coagulated with injection of steam. The pressed cake is sent to the dehydrator. The coagulated juice is then sent to a separator where the soluble fraction is separated from the green curd and moved to the evaporator where it is concentrated to 50% by volume. The curd is sent to the drier to produce the cassava protein concentrate which is 50% protein (Müller 1977).

Production of single cell protein from cassava

The use of cassava as substrate for single cell protein has been investigated since the mid-1960s. Gray and Abou-El-Seoud (1966) grew some filamentous fungi on ground cassava

roots, supplemented with ammonium chloride and corn steep liquor, to obtain biomass containing 13-24% crude protein.

Shrassen *et al*. (1970) described a process in which the yeast *Candida utilis* fermented enzymatically hydrolyzed cassava in a submerged culture to produce a product containing 35% crude protein on a dry weight basis. Gregory (1977) using *Aspergillus fumigatus* 1-21 A fermented whole cassava in a nonaseptic continuous fermentation system to produce single cell protein containing 37% crude and 27% true proteins. The fungi was a nonrevertible sporogonous mutant of *A*. *fumigatus* 1-21. This product was fed to rats and it produced good growth responses.

Single cell protein can be produced by two types of fermentation processes, namely submerged fermentation and semisolid state fermentation (Figure 3).

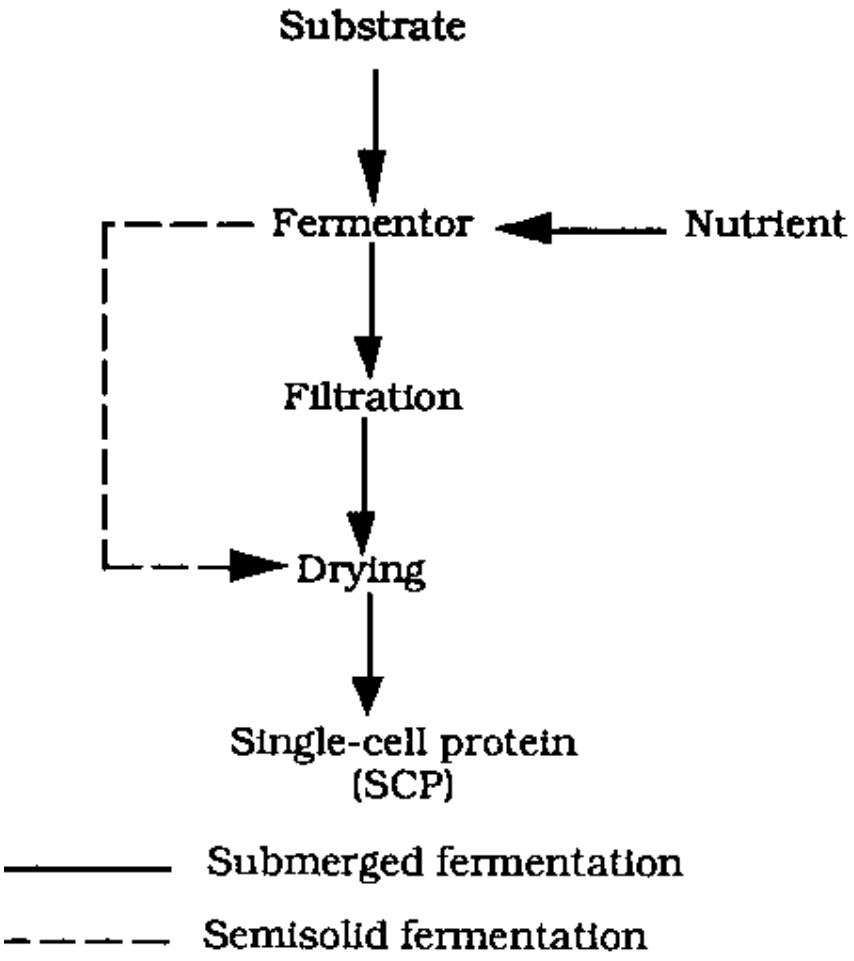

Figure 3: Flow chart for single-cell protein production (Hahn *et al.*, 1988)

2.2 Textile and Art

Starch is a popular textile material which can be produced from cassava. Cassava roots are peeled, washed and grated. The grated pulp is steeped for 2-3 days in a large quantity of water, stirred and filtered through a piece of cloth. The filtrate stands overnight and the supernatant is then decanted. The starch sediments are air-dried under shade.

In 1811, Kirchoff discovered that sugar could be produced by the acid hydrolysis of starch. Glucose, or dextrose sugar, is found in nature in sweet fruits such as grapes and in honey. It is less sweet than sucrose (cane or beet sugar) and also less soluble in water; however, when used in combination with sucrose, the resulting sweetness is often greater than expected.

The commercial manufacture of glucose sugars from starch began during the Napoleonic Wars with England, when suppliers of sucrose sugar were cut off from France by sea blockade. Rapid progress was made in its production in the United States about the middle of the nineteenth century.

At present, glucose is usually produced as syrup or as a solid. The physical properties of the syrup vary with the dextrose equivalent (DE) and the method of manufacture. Dextrose equivalent is the total reducing sugars expressed as dextrose and calculated as a percentage of the total dry substance. Glucose is the common name for the syrup and dextrose for the solid sugar. Dextrose, sometimes called grape sugar, is the D-glucose produced by the complete hydrolysis of starch.

2.3 Mineral Processing – Gold extraction using cassava solution

Cyanidation is a process for the extraction of gold from ores and was first developed by MacArthur Forrest in 1887. Since then, it has become the principal method of extracting gold from ores. In this process, the ore is crushed to a very fine powder. Such powdered ore is heaped onto open-air leach pads put on a base of asphalt or impervious plastic sheeting. A dilute solution of cyanide, usually sodium cyanide, is sprayed through sprinklers on the heap. The cyanide solution percolates down through the heap for several weeks, forming cyano gold complexes. This solution, enriched with gold, gets collected at the bottom into the pond termed as pregnant pond, from which it is pumped to the recovery plant. In the recovery plant, the solution containing cyano-gold complex is filtered off and the remaining rock pulp is separated. Zinc dust is then added to the solution containing cyano-gold complex to reduce the gold (III) oxidation state to zero oxidation state (metallic state). Gold is thus precipitated out as a high grade concentrate. Gold precipitate is then refined to get high purity gold. The perfection of the cyanide process largely replaced amalgamation process.

This has proved to be an economical process even for the extraction of gold from low grade deposits in spite of the low recovery (60% - 70%) of gold. The method is preferable to amalgamation because the spent cyanide solution discharged as effluent is biodegradable.

2.4 Surface Modification (Surface Strengthening)

Pack-cyaniding of mild steel using cassava leaves and the characterization of the case formed have been reported. Cassava contains some amount of cyanide that is often removed as waste during processing. Researchers have devised means of converting this wanton cyanide waste to engineering value via a clean technology technique thereby making it of benefit to human use.

Fresh cassava leaves of specie *Manihot esculenta (bitter local variety)* were collected, oven-dried, pulverized and subjected to sieve analysis to produce the required particle size. Required particle size are mixed with $BaCO_3$ salt by combining 4 volumes of cassava powder with 1 volume of $BaCO_3$ Salt. A firm fireclay luting is provided at the slits between the cyaniding boat and its cover plate. Mild steel sample completely embedded in the cyaniding boat is loaded into a muffle furnace at room temperature. The furnace is heated to 950 ^oC and held for sufficient time depending on the sample thickness and case depth required. The samples can then be cooled in air or quenched in water/oil as the case may be. This process is called high temperature pack cyaniding. The process is the same for low temperature pack cyaniding except that the energizer is now $BaCl_2$ salt and heat treatment temperature is 550^oC.

DISCUSSION

Cassava ~~(*Manihot esculenta crantz*)~~ is one of the most important food crops grown in the tropics (Hahn *et al*., 1988) and a significant source of calories for more than 500 million people world-wide. The production of cassava for human consumption has been estimated to be 65% of cassava products, while 25% is for industrial use, mostly as starch (6%) or animal

feed (19%) and 10% lost as waste (Anjos *et al.*, 2014). The production has significantly improved with Nigeria as the largest producer and garri is the most consumed and traded of all the food products from cassava roots in Nigeria (Uvere and Nwogu, 2011) and in many other countries in West Africa. It is creamy-white, partially gelatinized roasted free flowing granular flour. It is wide consumption is attributed to its relatively long shelf life compared to other food products from cassava, as well as its ease of preparation for eating.

Cassava is a major raw material used in many industries in Thailand. It is used in the production of Monosodium glutamate and other amino acids, sweeteners, ethanol, etc. Large cassava wastes are obtained from these production processes (containing a high amount of starch) and are used mainly as animal feed. These cassava wastes can still be utilized to produce ethanol due to its containing cellulose and hemi-cellulose at levels of 24.99 and 6.67 % (by weight) respectively (Teerapatr *et al.*, 2008). The use of cassava waste as raw material in ethanol production not only reduces waste material created from the cassava starch industry, but also lowers the cost of ethanol production (Akpan *et al.*, 2004). Presently, more than 60% of cassava produced in China is used for industrial purposes, 30% is used for animal feed and only 10% is used for human food (Wenquan, 2008).

Cassava is particularly suitable for production of modified starch. Modified starch is a main product among starch derivatives because it has become a new raw material in multiple industries. For example, modified starch is the third most important material in the paper making industry, and large amounts are also used in the textile industry (Wenquan, 2008).

Production costs are lower for cassava than for alternative food staples. Available farm management data indicate that labor constitutes 80 percent or more of production costs in smallholder cropping systems in Nigeria. Cost of production per metric ton (MT) is lower for cassava when compared with alternative food staples.

The pre-process storage is the main problem of cassava utilization on an industrial scale. Physiological deterioration occurs in cassava roots 2-3 days after harvesting, followed by microbial deterioration 3-5 days thereafter (Coursey, 1973). This deterioration is either primary deterioration, which is characterized by the discoloration of roots or microbial deterioration. The starch also undergoes structural changes. Economically, the roots discoloration is more important than the microbial deterioration because it reduces the economic value of the roots and most especially for production of gari and fufu.

Several modern storage methods have been developed to control the deterioration like refrigeration, freezing, waxing and chemical protection. While the traditional methods include leaving roots in the soil after maturity, burial of freshly harvested roots, storing in trench etc. However, most of the modern methods may not be economically viable for storing of cassava roots prior to processing to major products like gari and fufu.

At present most of the dextrose in commerce is prepared in the form of pure dextrose monohydrate by a combined acid-enzyme process. The hot, thick glucose syrup with a concentration of 70-80 percent dextrose is run from the evaporator into crystallizing pans. Crystal formation is largely controlled by the quantity of dextrins left with the glucose. The separation of crystals from the syrup is carried out in centrifugal separators and the impurities are left in the mother liquor. Crystalline dextrose is then dried in rotary hot-air driers under vacuum and bagged in moisture-proof materials.

Recrystallization of dextrose will yield practically 100 percent pure dextrose crystals which are used as a pharmaceutical-grade sugar.

The starch used in the manufacture of glucose syrup must be as pure as possible with low protein content (particularly soluble protein). In this respect, cassava starch can be preferable to other starches.

There is an increasing interest in manufacturing glucose syrup directly from starchy roots or grains rather than from the separated starch in order to save on capital investments for the production and purification of starch from such raw materials.

The starch conversion industry (glucose and dextrose) is the largest single consumer of starch, utilizing about 60 percent of total starch production. Glucose syrup and crystalline dextrose compete with sucrose sugar and are used in large quantities in fruit canning, confectioneries, jams, jellies, preserves, ice cream, bakery products, pharmaceuticals, beverages and alcoholic fermentation.

The functional purpose of glucose and dextrose in the confectionery industry is to prevent crystallization of the sucrose; in the bakery products industry it is to supply fermentable carbohydrates; and in the ice-cream, fruit-preserves and similar industries it is to increase the solids without causing an undue increase in the total sweetness, thus emphasizing the natural flavour of the fruit, and also to prevent the formation of large ice crystals which mar the smooth texture.

In general, glucose and dextrose are used in the food industry as a partial or complete substitute for sucrose. The use of dextrose has increased in recent years in the food-processing industries.

Recent years have witnessed a tremendous growth in the number of gold-catalyzed highly selective chemical transformations (Arcadi and Di Giuseppe, 2004). The catalysis of organic reactions by gold compounds has been shown to be a powerful tool in organic synthesis (Thompson, 1999). Although gold was considered to be an inert metal for a long time, its ability to behave as a soft Lewis acid has only been recognized recently. Such a property allows gold to activate unsaturated functionalities such as alkynes, alkenes, and allenes to create carbon-carbon and carbon–heteroatom bonds under extremely mild conditions (Georgy *et al*., 2005; Balme *et al*., 2003). Moreover, by pre-coordination gold may activate sp, sp^2,

and sp^3 carbon–hydrogen bonds efficiently. This may provide new opportunities in organic chemistry using gold as a catalyst.

Gold nanoparticles are useful in the construction of electrochemical immunosensors where it plays a crucial role both in the enhancement of the electrochemical signal transducing the binding reaction of antigens at antibody immobilized surfaces and in the ability of increasing the amount of immobilized immunoreagents in a sTable mode. Hepatitis B virus surface antigen was detected using electrochemical impedance spectroscopy (EIS) through immobilization of the antibody onto gold nanoparticles-modified 4-aminothiophenol self-assembled monolayers (Wang *et al*., 2004). Potentiometric and amperometric immunosensors for Hepatitis B virus surface antigen detection were also constructed by electrostatic adsorption of the antibody onto gold nanoparticles/tris (2, 2-bipyridyl) cobalt (III) multilayer films (Tang *et al*., 2005) and by immobilization of the antibody onto gold nanoparticles-modified thiol-containing sol–gel network (Tang *et al*., 2006). The antigen–antibody reaction is detected through measuring the changes in the electric potential before and after.

Gold nanoparticles have been used in the assembly of electrochemical and amperometric biosensors for the diagnosis of patients with germ cell tumors and hepatocellular carcinoma. This is done by the detection of a tumor marker, alpha-fetoprotein (AFP), an on cofetal glycoprotein (Ying *et al*., 2005). Carbohydrate antigen 19-9 (CA19-9) is one of the most important carbohydrate tumor markers expressed in many malignancies as pancreatic, colorectal, gastric and hepatic carcinomas (Reetz *et al*., 2003).

Gold nanoparticle-modified electrodes are used in the assembly of electrochemical DNA biosensors. They constitute useful analytical tools for sequence-specific DNA diagnosis and detection due to their inherent advantages of low cost, sensitivity and rapidity of response (Odenthal and Gooding, 2007). An important associated aspect is the accurate, sensitive and rapid detection of the transgenic plants. DNA electrochemical sensors are most likely to

become an analytical tool for the transgenic plant products. Gold nanoparticles-modified electrodes represent DNA electrochemical biosensor and are described as accurate, rapid and sensitive for the electrochemical impedance spectroscopy detection of the sequence-specific DNA related to transgene in the transgenic plants. These DNA-modified gold electrodes are useful electrochemical genosensors for gene analysis, detection of genetic disorders, tissue matching, and forensic applications due to their high sensitivity, small dimensions, low cost and compatibility.

Gold nanoparticles exploit their unique chemical and physical properties for transporting and unloading the pharmaceuticals. First, the gold core is essentially inert and is their ease of synthesis; monodisperse nanoparticles can be formed with core sizes ranging from 1 to 150 nm (Connor *et al*., 2005). Second advantage is imparted by their ready functionalization, generally through thiol linkages. In addition, their photophysical properties could trigger drug release at remote place (Skirtach *et al*., 2006).

Drug Delivery Systems (DDSs) provide positive attributes to a 'free' drug by improving solubility, in vivo stability, and biodistribution. They can also alter unfavorable pharmacokinetics of some 'free' drugs. Moreover, huge loading of pharmaceuticals on DDSs can render 'drug reservoirs' for controlled and sustained release to maintain the drug. Hong *et al.* (2006) have demonstrated cellular delivery and glutathione-mediated, GSH-mediated release of a hydrophobic dye (BODIPY), as a model of hydrophobic drugs, using functionalized gold nanoparticles (fGNPs).

Surface strengthening processes of carburizing, nitriding, carbonitriding, cyaniding, etc, in order to have materials treated for service properties require the use of expensive reagents, most of which are currently being imported into Nigeria. Thus most of the components fabricated locally hardly go through these post-fabricated treatments, leading to frequent replacements of such components. The conventional mode of cyaniding involves the use of

the salts of the cyanides and cyanates which are very toxic. The present process, which makes use of waste cassava peels and leaves, reduces the toxic impact of cyaniding on the personnel as well as the environment. In addition, the process utilizes waste and converts it to wealth thus affording cost savings to consumers thereby promoting local content initiatives. The major drawback of cyaniding is the poisonous nature of cyanide and the process is only applicable to low carbon steel materials. In small and medium scale enterprises, salt bath treatment is the commonest method probably because of its relatively low cost and reduced treatment time. Unfortunately, substantial amount of highly toxic, corrosive and environmentally unfriendly gases are liberated from the fused salt mixture into the atmosphere. The disposal of the spent salt mixture is also hazardous to both the flora and fauna of the environment. Liquid salt bath nitriding in cyanide-cyanate baths tends to release toxic greenhouse gases like CO, CO_2, HCN, HCl and so on into the atmosphere. Both the salt composition and by-products are very toxic (Akinluwade *et al*., 2012).

5.0 CONCLUSION

This review study concludes as follows

1. Cassava (plant and products) has both agricultural and engineering value
2. Cassava plant contains cyanogenic glucoside which produces toxic cyanide by enzymatic action
3. Earlier research efforts concentrated on reducing the cyanide content thereby diminishing the engineering value of cassava
4. Current research efforts have unveiled a vast number of engineering applications for the toxic cyanide content present in cassava (especially in the leaves and tuber bark)

5. A large number of cassava wastes are now being harnessed via a waste-to-wealth clean technology process to create engineering values
6. The following are some of the ongoing research works on the engineering applications of cassava:

i. Synthetic isolation of cyanide from cassava – Conversion of cyanide to metallic salt
ii. Formulation of organo-stabilized pack-cyaniding powder and pellets
iii. Advanced Materials Production – Production of gold nanoparticles

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