EFFECT OF STIRRING ON THE DETOXIFICATION RATE OF CASSAVA MASH AT 30^0C

BY

BAKARE SHERIFF A.
2003/15094EH

DEPARTMENT OF CHEMICAL ENGINEERING

SCHOOL OF ENGINEERING AND ENGINEERING TECHNOLOGY

FEDERAL UNIVERSITY OF TECHNOLOGY, MINNA, NIGER STATE, NIGERIA.

NOVEMBER, 2008

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IN PARTIAL FULFILMENT OF REQUIREMENT FOR THE AWARD OF BACHELOR OF ENGINEERING (B. Eng)

NOVEMBER, 2008

DECLARATION

I, Bakare Sheriff, hereby declare that this research project, "Effect of stirring on the detoxification rate of cassava mash at 30^0c", carried out under the supervision of Professor J.O Odigure and presented in partial fulfilment of the requirement for the award of Bachelor of Engineering (B. Eng.) degree in Chemical Engineering has not been presented for any degree elsewhere, to the best of my knowledge.

Bakare Sheriff

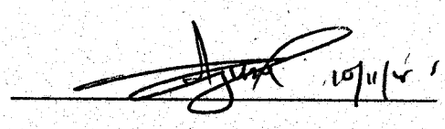
(2003/15094EH)

10-11-2024

Date

CERTIFICATION

This is to certify that this research project titled "Effect of stirring on the detoxification of cassava mash at 30^0c" was carried out by Bakare Sheriff (2003/15094EH) and submitted to the Department of Chemical Engineering, School of Engineering and Engineering Technology, Federal University of Technology, Minna, Niger State, in partial fulfilment of the requirement for the award of Bachelor of Engineering (B. Eng.) degree in Chemical Engineering.



Professor J.O Odigure _____ **Date**

(Project Supervisor)

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Dr .M.O Edoga **Date**

(Head of Department)

_____ _____

External Examiner **Date**

DEDICATION

To the Almighty Allah who has sustained me…

ACKNOWLEDGEMENT

I say Alhamdulillah to Almighty Allah, for his mercy, his grace and loving kindness, for guiding and protecting me through this programme. The master maker, life giver, the beginning and the end, You are Holy OH Allah, none is like you, you are the greatest.

I acknowledge with appreciation the immense contribution of my supervisor Professor J.O Odigure, who personally assisted in my research project making it possible for approval and his encouragement through it.

My appreciation goes to The Head of Department, Dr M.O Edoga and all lecturers of chemical engineering who have been a part of my success story and for their great impact on my life. Thank you all.

To my parents, Alhaji M.O and Hajia M.I Bakare for their immeasurable love, care, encouragement and support who denied themselves of many things just to make sure my future is made brighter I wouldn't trade you for the whole world. My siblings; Kike, A.K, Hafiz, and Maryam, what more can I say, I love u all.

To my cousins Sis B, Mama J, Kato, Jokky, Bunmi Salawu, Bunmex, Oke Sexy, Bolaji, Balogs, Busola, B Banj, Kemo, Guze, Dami,T-pain and Skenny, you are the greatest team in the whole world.

To my mothers; Mrs. S.W Aziza and Mrs S.I Balogun thank you for your unending contribution towards my success, May the Almighity bless you. To my uncles and aunties too numerous to mention, I appreciate your efforts, thank you dearly.

I wish to recognize my wonderful and invaluable friends, Ahmed B(chop moni), Segun A. (Nigga's P), O.J Ariyo (Tubaba), Bode Aji.(Lintuse), Jay, Ucixx, Blaze, Joey, Wolly D, Chudi P, Tobi, Sani Tiger, Romantic Roro, Jabooz, Guvnor, Banky, Bashie, Tunde Papien, Ay, Bjay, T girl and a host of others that I didn't mention.

To Tinuola Oladuntoye, thank you for everyday and everything.

To the entire Chemical Engineering Department, you have been a major part of a dream come true and it's a pleasure being part of you.

ABSTRACT

This research work deals with the effect of stirring on the detoxification rate of cassava mash at 30°c using cassava as raw material. The constraints of processing cassava are labour hour and the reduction or elimination of the cyanide level to the acceptable threshold limit. Thus, it has become necessary to study the process chemistry of cassava and work on the weak points so as to upgrade the existing technologies on detoxification. To achieve this, two experiments were carried out. Cassava roots were peeled and grinded into a mash, 100g was weighed out and moisture content determined to be 59.3% which was compared to the theoretical value of 60 – 70%. 100g of fresh cassava mash was weighed and mixed with 59.3ml of water to form a ratio of 1:1 with the cassava mash water ratio and heated at detoxification temperature of 30°c and 40°c at a different retention time with constant stirring. The result showed that acidity of the solution increased with retention time and it was clear that the more the retention time with stirring the lesser the toxicity of cassava mash. It also showed that the moisture content calculated of cassava mash was found to be close in range to the expected moisture content of cassava mash.

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CHAPTER ONE

1.1 INTRODUCTION

Cassava is the fourth most important food crop in the tropics. It is also known as Manihot Esculenta Crantz and its popularity has grown because it is now consumed in most parts of the world.

Around the world, it is a vital staple for about 500 million people and an efficient source of low cost carbohydrates, important for food security particularly in Africa and as an industrial raw material especially in Asia and Latin America. Its importance as livestock feed and in the starch, alcohol, textile and pharmaceutical industries cannot be over emphasized.

Its major disadvantage is that it contains cyanogenic glucosides which liberate hydrogen cyanides. Cyanogenic glucosides are a group of widely occurring natural substances that on hydrolysis yield a ketone, a sugar and highly toxic cyanide ion. Other toxins contained in cassava are linamarin and lotaustralin. It is believed that in humans, linamarin can be broken down by linamarase found in the bacteria that resides in the intestinal track resulting in the release of hydrogen cyanide which is a colourless gas with a faint bitter almond-like odour. The residential linamarin and its breakdown products should be removed during food processing.

Various communities using cassava as food in different forms have always used various processing methods to obtain cassava seemingly free of harmful amount of cyanogenic glucosides including chopping, heating and grinding (Charles 2001). Studies have shown that food items prepared by these methods still contain varying amount of residual cyanogenic glucosides (Oke, 1966; Wood, 1965).

Another feature that could enhance detoxification is the size of the cassava chips; large particle size will ensure the retention of more starch, increase the drying time and decrease surface area available for enzymic activities. Small surface however has the reverse effect (Odigure 1995).

Fermentation is the favorite method for detoxification of cassava since the plant naturally contains cyanogenic glucosides as well as for improvement and stabilization of nutritional and organoleptic quality of the products.

1.2 AIMS AND OBJECTIVES

(1) To study detoxification rate of cassava

(2) To be able to determine detoxification rate for different temperatures for different stirring time.

1.3 LIMITATIONS

The use of cassava in some places has been limited due to the presence of cyanogenic glucosides, deficiency in nutrients other than energy, dustiness of dried products etc. Nevertheless, it helps a lot i.e., it would help guarantee the supply of energy in these regions. As presence of cyanogenic glucosides constitute a major limitation to the use of cassava both in human and animal foods, there is need to review current findings for the elimination of the toxic glucoside in cassava products.

CHAPTER TWO

LITERATURE REVIEW

2.1 CASSAVA AS A FOOD CROP

Cassava is a shrubby, tropical, perennial plant that is not well known in the temperate zone. The plant grows tall, sometimes reaching 15 feet with leaves varying in shape and size. The tuber is dark brown and grows up to 2 feet long.

Cassava is a high energy producing tuber crop consisting mainly of starch which belongs to the family of Euphorbiaceae, a specie of Manihot Esculenta Crantz. It has common names like Yuca, Tapioca and Manioc. The plant is extremely tolerant to climatic stress, is mainly cultivated in humid tropics and is available throughout the year. Africa is one of the largest producers worldwide of cassava (50 million tons annually).

Cassava thrives better in poor soils than any other major food plant. As a result, fertilization is rarely necessary. However, yields can be increased by planting cuttings on well drained soil with adequate organic matter. Cassava is a heat-loving plant that requires a minimum temperature of 80 degrees F to grow. Since many cultivars are drought resistant, cassava can survive even during the dry season when the soil moisture is low, but humidity is high.

Cassava is consumed mainly in fermented forms. Garri and Attieke are the main fermentation products produced in cassava growing countries in Africa, Garri in Nigeria while Attieke in Cote d' Ivoire. The cassava plant gives the highest yield of food energy per cultivated area per day among crop plants. Cassava roots contains significant amount of Calcium, Phosphorus and Vitamin C. However, they are poor in protein and other nutrients. In contrast, cassava leaves are a good source of protein if supplemented with the amino acid methiomine.

2.2 HISTORY OF CASSAVA

Cassava was domesticated sometime in the distant past, maybe five thousand years ago. Exactly where is not known, but the current consensus is that domestication took place

somewhere in Central or South America, perhaps along the southern border of Brazil, where wild relatives of cassava are currently found.

Cassava was the staple food crop of the Amerindians of South America when the Portuguese arrived in 1500 just south of what is known as Bahia, Brazil. The Amerindians living in the area were the Tupinamba, who relied on cassava as a dietary staple, processing it into bread and meal using techniques similar to those still used by Amerindians in the twenty-first century.

When the Portuguese began to import slaves from Africa in about 1550, they used cassava in the form of meal to provision their ships and began cultivating cassava at their stations along the coast of West Africa soon afterward. From their stations near the mouth of the Congo River, cassava diffused to all Central Africa. The Portuguese were also responsible for introducing cassava to East Africa, Madagascar, India, Ceylon, Malaya and Indonesia by the 1700s.

Cassava was first introduced into Asia during Spanish occupation of the Philippines and was distributed throughout tropical Asia by the beginning of the nineteenth century. Expansion of cassava cultivation was pushed by colonial administrators who saw cassava as a famine reserve (especially the Dutch in Java and the British in India) and as an export commodity (Malaya and Java in the 1850s).

2.3 PROCUREMENT AND PRODUCTION OF CASSAVA

Cassava is typically grown by small scale farmers using traditional methods and farming on marginal lands not well suited to other crops. It is propagated by planting stakes cut from the woody stem of mature plants. These plantings require adequate moisture during the first two to three months, but after that they are relatively drought resistant. Cassava roots mature to harvestable size in six to twelve months depending on variety and ecological conditions and can be harvested at any time in the following two years.

2.3.1 HARVESTING OF CASSAVA

Most cassava is harvested by hand, lifting the lower stem and pulling the roots out of the ground then removing them from the base of the plant by hand. The upper parts of the stem with the leaves are removed before harvest. Leaves and ropes can be used to assist harvesting.

A mechanical harvester has been developed in Brazil. It grabs onto the stem and lifts the roots from the ground. Care must be taken during the harvesting process to minimize damage to the roots, as this greatly reduces shelf life. During the harvesting process, the cuttings for the next crop are selected. These must be kept in a protected location to prevent desiccation.

2.3.2 PROCESSING

The shelf life of cassava is only a few days unless the roots receive special treatment. Removing the leaves two weeks before harvest lengthens the shelf life to two weeks. Dipping the roots in paraffin or a wax or storing them in plastic bags reduces the incidence of vascular streaking and extends the shelf life to three to four weeks. Roots can be peeled and frozen. Traditional methods include packing the roots in moist mulch to extend shelf life.

Dried roots can be milled into flour. Maize maybe added during the milling process to add protein to the flour. The flour can be used for baking breads. Roots can be peeled, grated and washed with water to extract the starch which can be used to make pasta and pearls of tapioca. Unpeeled roots can be grated and dried for use as animal feed. The leaves can add protein to animal feed.

2.4 USES OF CASSAVA

Cooked in various ways, cassava is used in a great variety of dishes. The soft-boiled root has a delicate flavor and can replace boiled potatoes in many uses: as an accompaniment for meat dishes, or made into soups, stews etc. Tapioca and Fufu are made from the starchy cassava

root flour. Tapioca is an essentially flavourless starchy ingredient or fecula produced from treated and dried cassava root and used in cooking.

The juice of the bitter boiled to the consistence of thick syrup and flavoured with spices is called cassareep. It is used as a basis for various sauces and as a culinary flavouring, principally in tropical countries. The leaves are pounded to a fine chaff and cooked as a palaver sauce in Sierra Leone, usually with palm oil but vegetable can also be used. Palaver sauces contain meat and fish as well. In many countries significant research has begun to evaluate the use of cassava as an ethanol biofuel.

2.4.1 USES IN AFRICA

Nigeria is the world's largest producer of cassava. In West Africa, particularly in Nigeria and Sierra Leone, it is commonly prepared as Eba or Garri. The cassava is grated, pressed, fermented and fried then mixed with water to form a thick paste (Eba). Historically, people were economically forced to depend on cassava risk chronic poisoning diseases such as Tropical Ataxic Neuropathy (TAN) or such malnutrition diseases such as kwashiorkor and endemic goitre.

In Central Africa, cassava is traditionally processed by boiling and mashing. The resulting mash can be mixed with spices then cooked further or stored. A popular snack is made by marinating cassava in salted water for a few days then grilling it in small portions. Many cassava dishes exist in various African countries.

In Tanzania, cassava is known as Mihogo. Though customs vary from region to region and the methods of cooking cassava vary accordingly, the main method is simply frying it. The fried cassava is a very common street food as it is relatively cheap to buy, easy to prepare and good to eat. In Zambia, Ugali a porridge more akin to mashed potatoes is known as Nshima. In Kenya, the Kikuyu name for it is Mwanga.

Residents in the sub – Saharan nation of the Central African Republic, have developed multiple unique ways of utilizing the abundant cassava plant.

2.4.2 ETHNOMEDICAL USES

The bitter variety of cassava root is used to treat diarrhea and malaria. The leaves are used to treat hypertension, headache and pain. Cubans commonly use cassava to treat irritable bowel syndrome, the paste is eaten in excess during treatment.

2.4.3 CASSAVA AS ANIMAL FEED

Cassava is used as animal feed in Asia, South America, Africa and Europe especially in places such as Thailand, China, Nigeria, Brazil etc.

2.4.4 CASSAVA HAY

Cassava hay is hay which is produced at a young growth stage, 3-4 months and being harvested about 30-45 cm above ground, sundried for 1-2 days until having final dry matter of at least 85%. The cassava hay contains high protein content, 20-25% and condensed tannins, 1.5-4%. It is used as a good roughage source for dairy, beef, buffalo, goats and sheep by either direct feeding or as a protein source in the concentrate mixtures.

2.4.5 CASSAVA PEST

In Africa, the cassava mealy bug and cassava green mite can cause up to 80%crop loss, which is extremely detrimental to the production of subsistence farmers. These pests were rampant in the 1970s and 1980s but were brought under control following the establishment of the Biological Control Centre for Africa of the International Institute of Tropical Agriculture (IITA). The centre investigated biological control for cassava pests; two South American natural enemies Typhlodromalus lopezi (a parasitoid wasp) and Typhlodromalus aripo (a predatory mite) were found to effectively control the cassava mealy bug and the cassava green mite respectively.

The cassava mosaic virus causes the leaves of the cassava plant to wither, limiting the growth of the root. The virus is spread by the whitefly and by the transplanting of diseased plants into new fields. Sometime in the late 1980s, a mutation occurred in Uganda that made the virus even more harmful, causing the complete loss of leaves. This mutated virus has been spreading

at a rate of 50 miles per year and as of 2005 may be found throughout Uganda, Rwanda, Burundi, The Democratic Republic of Congo and the Republic of Congo.

2.5 CHEMICAL COMPOSITION OF CASSAVA

Study of cassava chemistry has shown that cassava root is composed of several substances

Substances	% Composition
Moisture	69.80
Starch	22.00
Sugar	5.10
Protein	1.10
Fat	0.40
Fibre	1.10
Ash	0.50

2.6 TOXICITY

The leaves cannot be consumed raw since they contain free and bound cyanogenic glucosides. These are converted to cyanide in the presence of linamarase, a naturally occurring enzyme in cassava. The roots however are eaten raw everywhere in Africa. Cassava varieties are often categorized as either sweet or bitter signifying the absence or presence of toxic levels of cyanogenic glucosides. The so called sweet cultivars can produce as little as 20 milligrams of cyanide per kilogram of fresh roots while bitter ones may produce more than 50 times as much. Cassava grown during drought is especially high in toxins. One dose of pure cassava cyanogenic glucosides (40mg) is sufficient to kill a cow.

Societies which traditionally eat cassava generally understand that soaking and/or cooking is necessary to avoid getting sick. However, problems do occur. Dr Jasson Ospina, an Australian plant chemist has developed a simple method to reduce the cyanide content of cassava

flour. The method involves mixing the flour with water into a thick paste and then letting it stand in the shade for five hours in a thin layer spread over a basket, allowing an enzyme in the flour to breakdown the cyanide compound. The cyanide compound produces hydrogen cyanide gas which escapes into the atmosphere reducing the amount of poison by up to five-sixths and making the flour safe for consumption the same evening. This method is currently being promoted in rural African communities that are dependent on cassava.

For some smaller rooted sweet varieties, cooking is sufficient to eliminate all toxicity. The larger rooted bitter varieties used for production of flour or starch must be processed to remove the cyanogenic glucosides. The large roots are peeled and then ground into flour which is then soaked in water, squeezed dry several rimes and toasted. The starch grains that float to the surface during the soaking process are also used in cooking. The flour is used throughout the Caribbean. The traditional method used in West Africa is to peel the roots and put them into water for three days to ferment. The roots are then dried or cooked.

In Nigeria and several other West African countries including Ghana, Togo, Ivory Coast and Burkina Faso, they are usually grated and lightly fried in palm oil to preserve them. The result is a foodstuff called Gari.

2.7 NATURE OF CASSAVA TOXIN

Cassava is used both in the fresh and processed form. In the whole unbruised plant the cyanogenic glucoside remains intact in the form of linamarin and lotaustralin. When the cellular structure is disrupted, the intracellular glucoside becomes exposed to the extra cellular enzyme linamarase. Hydrocyanic acid is then produced. The reaction has been shown to proceed in two steps:

i) Cyanogenic glucoside is degraded to sugar and cyanohydrin

ii) Cyanohydrin then dissociates into ketone and hydrocyanic acid. Thus, for linamarin, the glucoside is first hydrolysed by linamarase to produce B-D glucopyranose and 2 – hydroxyisolentyronotrite or acetone – cyanohydrin after which the latter is degraded to acetone and HCN. Cyanohydrin produced as a result of linamarin activity is stable only under moderately acidic condition.

In spite of the relative instability of cyanohydrin, it coexists with intact glucoside and HCN in differently processed cassava products. It is therefore clear that cyanide in cassava produce exists in three forms

i) the glucosides (linamarin and lotaustralin)

ii) the cyanohydrin

iii) the free hydrocyanic acid (HCN)

2.8 CYANOGENESIS IN CASSSAVA

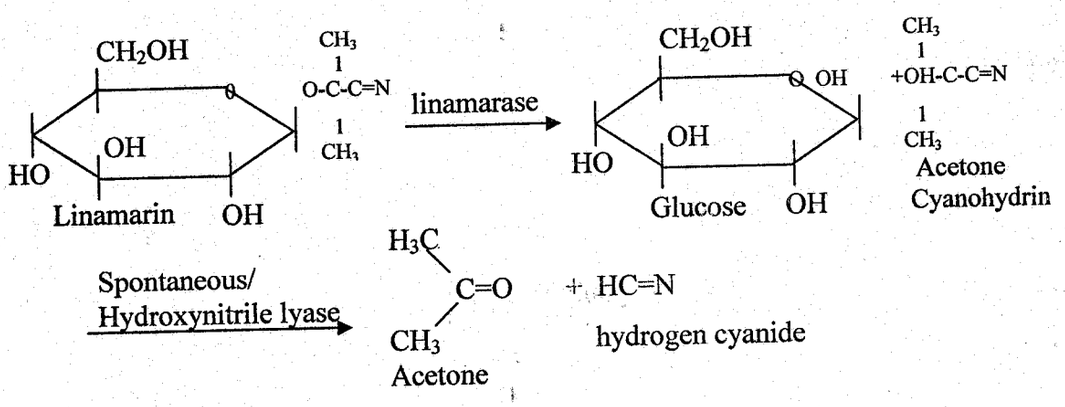
The cyanogenic glucosides are a group of nitrile – containing plant secondary compounds that yield cyanide (cyanogenesis) following their enzymatic breakdown. The functions of cyanogenic glucosides remain to be determined in many plants. However, in some plants they have been implicated as herbivore deterrents and as transportable forms of reduced nitrogen. It is estimated that between 3000 and 12000 plant species produce and sequester cyanogenic glucosides including many important crop species.

All cassava tissues, with the exception of seeds contain the cyanogenic glucosides linamarin (> 90% total cyanogen) and lotaustralin (< 10% total cyanogen). Leaves have the highest cyanogenic glucosides levels whereas roots have approximately 20 – fold lower linamarin levels. Total root linamarin levels range between 100 and 500mg linamarin 1kg fresh weight for low and high cyanogenic cultivars respectively.

Cyanogenesis is initiated in cassava when the plant tissue is damaged. Rupture of the vacuole releases linamarin which is hydrolysed by linamarase, a cell wall associated with glycosidase. Hydrolysis of linamarin yields an unstable hydroxynitrile intermediate, acetone cyanohydrin. Acetone cyanohydrin spontaneously decomposes to acetone and HCN at pH > 5.0 or temperatures > 35^0c and can be broken down enzymatically by HNL (Hydroxynitrile Lyase).

Various health disorders are associated with the consumption of cassava which contains residual cyanogens. These disorders include hyperthyroidism, tropical ataxic neuropathy. Cyanide poisoning from high – cyanogenic cassava is typically associated with insufficient consumption of Cys and met in the diet. Reduced sulfur containing compounds are substrates for the detoxification of cyanide catalysed by the enzymes rhodanese and/or B-

cyano-alanine synthise. Until recently, it had been assumed that all of the residual cyanogens present in cassava foods were in the form of linamarin. This assumption was based on the observation that acetone cyanohydrin is unstable and that the cyanide generated from acetone cyanohydrin is readily volatilized during food processing. Recently, however, it was demonstrated that the major cyanogens present in some poorly processed cassava roots was acetone cyanohydrin not linamarin. These results suggested that the spontaneous (high pH and /or temperature) and enzymatic breakdown of acetone cyanohydrin was reduced or inhibited in roots. In part, the high residual acetone cyanohydrin levels could be attributed to the low pH conditions established during the soaking of roots for food preparation. This hypothesis, however does not address the contribution of HNL activity to root acetone cyanohydrin turnover and root cyanogenesis.



2.8.1 CYANIDE

Cyanide is any chemical compound that contains the cyano group which consists of a carbon atom triple-bonded to a nitrogen atom. Cyanide specifically is the anion CN^-. Of the many kinds of cyanide, some are gases, others are solids or liquids. Those that can release the cyanide ion CN^- are highly toxic.

2.8.1.1 OCCURRENCE

Cyanides are produced by certain bacteria, fungi and algae and are found in a number of foods and plants. Cyanide is found although in small amounts in apple seeds, mangoes and almonds. In plants, cyanides are usually bound to sugar molecules in the form of cyanogenic

glucosides and serve the plant as defence against herbivores. Cassava (manioc) an important potato like food grown in tropical countries contains cyanogenic glucosides.

2.8.1.2 USES OF CYANIDE

The cyanide compound sodium nitroprusside is occasionally used in emergency medical situation to produce a rapid decrease in blood pressure in humans. The molecule of vitamin B12 usually also contains cyanide.

Gold and silver cyanide are among the very few soluble forms of these metals and cyanides are thus used in mining as well as electroplating, metallurgy, jewelry and photography.

Cyanides are illegally used to capture fish near coral reefs for the aquarium and seafood markets. The fishing occurs mainly in the Philippines, Indonesia and the Caribbean to supply 2 million marine aquarium owners in the world. Environmental organizations are critical of the practice as are some aquarists and aquarium dealers to prevent the trade of illegally caught aquarium fish.

Cyanides are used as insecticides for the fumigating of ships. They are also used as rat poison in some places.

2.8.1.3 TOXICITY OF CYANIDE

Many cyanide containing compounds are highly toxic but some are not. The most dangerous cyanides are hydrogen cyanide (HCN) and salts derived from it, such as potassium cyanide and sodium cyanide. Cyanide is as inhibitor of the enzyme cytochrome oxidase in the fourth complex of the electron transport chain.

Cyanides have been used as a poison many times throughout history. Its most infamous application was the use of hydrogen cyanide by the Nazi regime in Germany for mass murder in some gas chambers during the holocaust. It has also been used for murder as in the case of some notable figures; Erwin Rommel, Eva Braun, Adolf Hitler (in combination with gunshots) e.t.c.

2.8.1.4 CYANIDE DETOXIFICATION IN CASSAVA FOR FOOD USES

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. These methods consist of different combinations of peeling, chopping, grating, soaking, drying, boiling and fermenting. While all these methods reduce the cyanide level, the reported loss in cyanide content differs considerably due to analytical methods, the combination of methods and extent to which the processes are carried out. The specific effects of various processing techniques on the cyanide content of cassava are discussed below:

Peeling

Many methods of processing cassava roots commence with the peeling of the tubers. Generally the cassava peel contains higher cyanide content than the pulp. Removal of the peel therefore reduces the cyanogenic glucoside content considerably. In studies, cassava varieties are of two types i.e. sweet and bitter. The classification is based on the cyanide content; with the sweet varieties having almost cyanide in the cortex and skin and little or no cyanide in the pulp, whereas the bitter varieties, more or less have an even distribution of cyanide throughout the tuber. For these reasons, the former can be eaten boiled while the latter has to be processed before it can be consumed.

Peeling, therefore, can be an effective way to reduce the cyanide content by at least 50% in cassava tubers. However, it should be noted that while the peel contains a high glucoside content relative to the pulp, the glucoside level is higher in the latter.

Grating

This process takes place after peeling and is sometimes applied to whole tubers. Grating of the whole tuber ensures the even distribution of the cyanide in the product and will also make the nutrients contained in the peel available for use. In the grated product, the concentration of cyanide depends on the time during which the glucoside and the glucosidase interact in an aqueous medium.

Soaking

Soaking of cassava roots normally precedes cooking or fermentation. It provides a suitably larger medium for fermentation and allows for greater extraction of the soluble cyanide into the

soaking water. The process removes about 20% of the free cyanide in fresh root chips after 4 hours, although bound cyanide is only negligibly reduced. Bound cyanide begins to decrease only after the onset of fermentation. A very significant reduction in total cyanide is achieved if the soaking water is routinely changed over a period of 3 – 5 days.

A variation to the soaking technique known as retting was described by Ayenor (1985). This process involves prolonged soaking of cassava roots in water to effect the breakdown of tissue and extraction of the starchy mass. A simulation of the technique followed by sun drying showed a reduction of cyanide of about 98.6% of the initial content in the roots.

Boiling or Cooking

As with soaking, the free cyanide of cassava chips is rapidly lost in boiling water. About 90% of free cyanide removed within 15 minutes of boiling fresh cassava chips compared to a 55% reduction in bound cyanide after 25 minutes (Cooke and Maduagwu, 1978). Cooking destroys the enzyme linamarase at about 72% thus leaving a considerable portion of the glucoside intact.

Fermentation

Microbial fermentation have traditionally played important roles in food processing for thousands of years. Most marketed cassava products like garri, fufu, apu e.t.c in Africa are obtained through fermentation. The importance of fermentation in cassava processing is based on its ability to reduce the cyanogenic glucosides to relatively insignificant levels. Unlike alcoholic fermentation, the biochemistry and microbiology is only superficially understood, but it is believed that some cyanidrophic/cyanide tolerant microorganisms effect breakdown of the cyanogenic glucoside. It has been shown that the higher the retention of starch in grated cassava the better the detoxification process. Also the lower the fermentation process the lower the residual cyanide content.

In Nigeria, investigation of the effect of fermentation period on the residual cassava toxins is currently being carried out. As a preliminary stage, the use of starter cultures recovered from fermentation effluents is being tested to increase the conversion of substrate to product reduce

fermentation time. Generally, fermented cassava products store better and often are too low in residual cyanide content.

A process which can be described as dry fermentation is believed to occur in cassava peelings which are usually heaped for days in many parts of Africa, before feeding to ruminants. The process generates heat and mould growth is common. However, the measurement of HCN losses during such a process has not been documented.

Ensiling

The ensiling process causes the disintegration of the intact glucoside via marked cell disruption, drop in pH of ensiled medium and intense heat generation. Ensiled roots have been used for livestock feeding. Gomez and Valdiviesco (1988) reported that ensiling cassava chips reduced the cyanide content to 36% of the initial value after an ensiling period of 26 weeks. We have also found that about 98% of the free cyanide was lost by ensiling cassava roots with poultry litter for 8 weeks.

Drying

Since cassava roots contain about 61% water, coupled with the solubility of its cyanogenic glucoside component, the dehydration process results in a substantial reduction in the content of this toxin in the pressed pulp. Drying is carried out using solar radiation (sun drying) or Driers depending on economic viability. The process is achieved at varying temperature. Works done have shown that sun drying;

i) Results in a greater loss of total cyanide compared to laboratory oven – drying at 60°c for 48hours. Oven drying apparently affects the stability of linamarase which decomposes at 72°c

ii) Tends to produce greater loss of bound cyanide due to slower drying rate relative to oven drying

iii) Allows a longer contact period between the glucosidase and the glucoside in the aqueous medium

iv) Facilitates the continuation of the fermentation process

v) is cost effective but slow and often encourages the growth of mould and other micro organisms

Because of the poor microbiological properties of sundried cassava products, there is a need for quicker drying methods which will reduce or eliminate microbial proliferation ensure optical cyanide detoxification.

2.8.2 LINAMARIN

Linamarin is a cyanogenic glucoside found in the leaves and roots of plants such as cassava, limba beans. Upon exposure to enzymes and gut flora in the human intestine, linamarin and its methylated relative lotaustralin can decompose to the toxic chemical hydrogen cyanide; hence food uses of plants that contain significant quantities of linamarin are inhibited by extensive preparation and detoxification requirements ingested and absorbed linamarin is rapidly excreted in the urine and the glucoside itself does appear to be toxic.

Consumption of cassava products with low level of linamarin is widespread in the lowland tropics. Ingestion of food prepared from insufficiently cassava roots with high linamarin levels has been associated with dietary toxicity. However, toxicity is believed to be induced by ingestion of acetone cyanohydrin, the breakdown products of linamarin. Dietary exposure to linamarin has also been reported as a risk factor in developing glucose intolerance and diabetes, although studies in experimental animals have been inconsistent in reproducing this effect and may indicate that the primary effect is in aggravating existing conditions rather than inducing diabetes on its own.

The generation of cyanide from linamarin usually enzymatic and occurs when linamarin is exposed to linamarase, an enzyme normally expressed in the cell walls of cassava plants. Because the resulting cyanide derivations are volatile, processing methods that induce such exposure are common traditional means of cassava preparation; foodstuffs are usually made from cassava after extended blanching, boiling or fermentation. Food product made from cassava plants include garri, porridge – like fufu, the dough agbelima and cassava flour.

Recent research efforts have developed a transgenic cassava plant that stably down regulates linamarin product via RNA interference.

2.8.3 LOTAUSTRALIN

Lotaustralin is a cyanogenic glucosides found in small amount of cassava among other plants. It is structurally related to linamarin, another glucoside found in these plants and differ from it only by the presence of an extra methyl group. Both lotaustralin and linamarin may be hydrolysed by the enzyme linamarase to form glucose and a precursor to the toxic compound hydrogen cyanide.

2.8.4 LINAMARASE

This is defined as an enzyme in the plants which liberates hydrocyanic acid from a cyanogenic glucoside in the same plant. Boiling destroys the enzyme and renders the material usually safe.

Linamarase is also known as beta – D – glucoside, an enzyme found in the cell walls of many plants e.g. cassava. When a plant is chewed, it exposes the enzyme to compounds like linamarin and lotaustralin which release cyanide compounds that can be lethal to the eater. In humans, chronic toxicity is more likely than death. The action of enzyme is used by many cultivars to process cassava into an edible substance, the enzyme converts the cyanide containing compounds to acetone cyanohydrin which spontaneously decomposes to hydrogen cyanide which either dissolves readily in water or it is released into the air. Not all cyanide can be removed during the process.

2.9 DETOXIFICATION OF CASSAVA

Detoxification is one process of removing or transforming poison into something more important. It can also be the process of removing a toxic substance from something or counteracting its toxic effects.

Cassava is consumed as a staple in a large number of countries in the developing world. Its consumption is however associated with pathological disorders such as goitres, tropical ataxic neuropathy and cretinism (Ermans et al. 1980; Mlingi et al. 1992; Tylleskare et al. 1992). This is due to the presence in cassava of the cyanogenic glucosides linamarin and lotaustralin, which are degraded through enzymatic activities to produce the toxic factors, cyanohydrins and hydrogen cyanide (HCN). Cyanogenic glucoside levels in the cassava root vary widely, and can accumulate to concentrations as high as 500 mg/kg (McMahon et al. 1995). Cyanogenic

glucoside levels in cassava must therefore be quantitated in order to assess "bitterness" or the "cyanogenic potential" of cassava varieties. Linamarase enzymes isolated from the cassava peel are currently applied as diagnostic reagents in the screening of cassava varieties for "bitterness." Methodology used incorporates the enzymatic hydrolysis of cyanogenic glucosides, followed by colorimetric measurement of cyanide released (Cooke et al. 1979). The development of biosensors incorporating linamarase, for linamarin detection in cassava and cassava-based products has also been reported (Yeoh & Truong 1993; Tatsuma et al. 1996). Biosensors of this type are increasingly replacing the use of colorimetric assays for monitoring enzymatic reactions in foods.

Complete detoxification of "bitter" cassava varieties can feasibly be accomplished through the enzyme-catalyzed degradation of both cyanogenic glucosides and the cyanohydrins which result from their degradation. Linamarase enzymes located in the cell walls of the cassava root (Mkpong et al. 1990), catalyze the initial step in the breakdown of the cytoplasmic cyanogenic glucosides linamarin and lotaustralin, resulting in the release of cyanohydrins. These cyanohydrins are relatively stable under low pH conditions but decompose under conditions of high temperature and high pH (pH >5), to produce ketones and HCN. The destruction of cassava cyanogenic glycosides is primarily an endogenous phenomenon, although microbial β-glucosidases assist in linamarase degradation during fermentation processing (Anupe & Brauman 1995). Bacillus species (Amoa-Awau & Jakobsen 1995), lactic acid bacteria (Cohen 1994) Aspergillus and Fusarium strains of fungi, some Penicillium strains and some Trichoderma strains (Yeoh et al. 1995) have been shown to secrete linamarase activity, and are potential sources of microbial linamarases. Hydroxynitrile lyase (acetone cyanohydrin lyase) (Thayer & Conn 1981; Kojima et al.

Hydroxynitrile lyase (acetone cyanohydrin lyase) (Thayer & Conn 1981; Kojima et al. 1979; Hughes et al. 1994; McMahon et al. 1995; Cheskul & Chulvatnatol 1996; Wajant & Pfizenmaier 1996) an endogenous enzyme of the cassava root, catalyzes the breakdown of cyanohydrins produced as a result of linamarase activity, leading to the release of HCN . HCN thus released is readily removable by evaporation. Complete cyanohydrin degradation through the combined

activities of linamarase and the cyanohydrin-degrading enzymes, followed by evaporative removal of HCN, would preclude the exposure of individuals involved in the processing of "bitter" cassava varieties, to dangerously high HCN levels emitted during roasting or high temperature cooking. Exogenous addition of cyanohydrin-degrading enzymes should certainly be a consideration for upgrading processing of "bitter" cassava roots where financial and technological conditions permit.

2.9.1 DETOXIFICATION TECNOLOGICAL CONDITIONS

Cyanide detoxification is dependent on some technological condition;

Enzymatic Hydrolysis

The biochemistry and physiology of cyanogenesis in cassava has been well characterized. Rupture of the vacuole initiates cyanogenesis by releasing linamarin which is then hydrolysed by linamarase, a cell wall and lactifier localized B-glucosidase. The glycosylated product acetone cyanohydrin can spontaneously decompose at pH >5 or temperature >35°c or is enzymatically broken down by hydronitrile lyase in leaves to produce acetone and cyanide.

Heating of Free Cyanide

The cyanide generated during food processing vapourizes at about 28^0c. The technology involved must ensure detoxification of cyanide to a value of 2-3mg/100g as acceptable level. Free cyanide is a measure of the cyanide present as HCN or CN^- The free cyanide of cassava chips is rapidly lost in boiling water.

About 90% of free cyanide is removed within 15minutes of boiling fresh cassava chips compared to a 55% reduction in bound cyanide after 25minutes. This process is achieved at varying temperature (60-90°c). Cooking destroys the enzyme linamarase at about 72°c thus leaving a considerable portion of the glucose intact.

Concentration or Solubilization in Water

Soaking of cassava roots normally precedes cooking or fermentation. It provides a suitably larger medium for fermentation and allows for greater extraction of the soluble cyanide into the soaking water. The process removes about 20% of the free cyanide in fresh root chips after 4hrs. Cyanide concentration in raw water appears to be low. Moisture content of cassava roots is between 61-62.8%.

Flour has been produced by traditional techniques with retention of 1.5-3.2%. Methods which the use of grating and crushing are very effective in removing cyanide because of the intimate contact in the finely divided wet parenchyma between linamarin and the hydrolyzing enzyme linamarase which promotes rapid breakdown of linamarin to hydrogen cyanide gas that escapes into the air . Mixing cassava flour samples with water and standing at 30°c for 5hrs gives a 3-6 fold reduction in cyanide content (Bradbury 2006). Water rapidly swells the flour and allows contact between the cyanide containing compound, linamarin and the enzyme linamarase that catalyses the breakdown of linamarin to acetone cyanohydrin which then breaks down spontaneously to give hydrogen cyanide gas.

CHAPTER THREE

EXPERIMENTAL PROCEDURE

3.1 APPARATUS USED

Raw Material (Cassava)

Beakers

Conical Flask

Spatula

Thermometer

Weighing Balance

pH Meter

Knife

Blender

Distilled Water

Magnetic Stirrer

Desiccator

Electric Oven

Electric Heater

Raw Material (Cassava)

3.2 PRETREATMENT OF RAW MATERIAL

The fresh cassava was peeled to ensure that some percentage of cyanide present was reduced since peeling reduces the cyanide content by 50%. The peeled cassava was then cut into pieces and put into a blender so it can be further processed into cassava mash.

3.3 DETERMINATION OF MOISTURE CONTENT

100 grammes of cassava mash was weighed into a pre-weighed aluminium dry dish. The dish and its content were then transferred into an oven at a temperature of 40°c for hours . After certifying that the content was dried, it was now allowed to cool in a desiccator, after which it was weighed and then transferred into the oven and the same process is done until a constant weight was gotten. The moisture content was calculated as:

$$\% \text{ Moisture Content} = \frac{M_1 - M_2}{M_1 - M_0}$$

M_1 = weight of sample + dish before drying

M_2 = weight of sample + dish after drying

M_0 = weight of aluminium dish

3.4 REACTION PROCESS

After the moisture content of the cassava mash was determined to be 59.3%, 59.3ml of water was added to the mash so the ratio of cassava mash water ratio to water is 1:1. The slurry formed from water and cassava mash was poured into a conical flask and a magnetic stirrer was dropped into it. The conical flask with its content was placed on an electric heater set at a temperature of 30° and was allowed to stir constantly for different time of 30 minutes. After heating, it was allowed to cool and the pH of the sample was taken using a pH meter that was well standardized using buffer solutions. The same process was repeated for other samples for different time of 60, 90, 120, 150 and 180 minutes all at temperature of 30°c

The same procedure was done for other samples of same quantity as above but at a different temperature of 40°C under constant stirring speed for 30, 60, 90, 120, 150 and 180 minutes after which the pH was taken.

3.5 DETERMINATION OF pH

After the heating process, the cassava mash was cooled to a temperature as low as that of room temperature, the pH was then determined with the aid of a well standardized pH meter. The pH meter was calibrated using standard buffer 4.0 and 7.0 solutions.

CHAPTER FOUR

RESULTS AND DISCUSSION OF RESULTS

4.1 RESULTS

Table 1: Table showing relationship between retention time of cassava and the pH at temperature of 30°c.

Mass of cassava mash (g)	% moisture content of cassava mash	% of H_2O added	Retention time (mins)	pH Before	pH After	Change in pH	% Change in pH
100	59.30	100	30	6.44	6.43	0.01	0.15
100	59.30	100	60	6.44	6.41	0.03	0.46
100	59.30	100	90	6.44	6.40	0.04	0.62
100	59.30	100	120	6.44	6.38	0.06	0.93
100	59.30	100	150	6.44	6.36	0.08	1.24
100	59.30	100	180	6.44	6.33	0.11	1.71

Table 2: Table showing relationship between retention time of cassava and the pH temperature of 40°c.

Mass of cassava mash (g)	% moisture content of cassava mash	% of H_2O added	Retention time (minutes)	pH Before	pH After	Change in pH	% Change in pH
100	59.30	100	30	6.44	6.38	0.06	0.93
100	59.30	100	60	6.44	6.33	0.11	1.71
100	59.30	100	90	6.44	6.26	0.18	2.79
100	59.30	100	120	6.44	6.21	0.23	3.57
100	59.30	100	150	6.44	6.17	0.27	4.19
100	59.30	100	180	6.44	6.12	0.32	4.96

4.2 DISCUSSION OF RESULTS

Processing methods play an important role in effective removal of cyanogens glucosides and their degradation. Reduction in pH shows that this result is in agreement with the work of McMahon et al (1995) in which they concluded that at a pH > 5.0 following linamarin hydrolysis facilitate the decomposition of acetone cyanohydrin and thereby reduce toxicity of the food product.

From the experiment carried out, one can say temperature and timing have various importance on the detoxification rate of cassava mash. It was observed that there was a rapid reduction in pH values. A rapid decrease in pH values while total acidity increases is because of a mainly lactic acid production. From table 1, the heating of cassava mash was done for different retention times of 30, 60, 90, 120, 150, 180 minutes which gave rise to pH values of 6.43, 6.41, 6.40, 6.38, 6.36 and 6.33 respectively. It can be said that the pH dropped from an initial value of 6.44 to different values depending on the retention time used at constant stirring of mash. At this given rate, it is expected that the medium pH value will reduce to a lower value in a longer retention time which tells us that the processing time of cassava will reduce by some hours. The percentage change in pH values increased as the values of pH reduced. Percentage change in pH increased from 0.15% to 1.71% which goes to show that more toxic will be lost at a retention time of 180 minutes at a temperature of 30°c at constant stirring.

Table 2 also shows that the higher the temperature, the more the reduction in the pH value which leads to a change in the pH. At 40°c, doubling the mash water content at constant stirring for different retention times of 30, 60, 90, 120, 150 and 180 minutes, the pH values were 6.38, 6.33, 6.26, 6.21, 6.17 and 6.12 respectively. This goes to tell us that the more the heating, the more the reduction in pH values. There was also a significant increase in the percentage

change in the pH, from 0.93% to 4.96%. It is observed that the values gotten from this experiment tend toward the acidic region. Cassava has cyanogenic glucosides, linamarin and lotaustralin which are degraded through enzymatic activities to produce the toxic factors, cyanohydrins and hydrogen cyanide. These cyanohydrins which result from degradation are relatively stable under low pH conditions but decompose at high pH > 5 to produce ketones and HCN which is readily removable by evaporation. Leaching also removes HCN with the fluid.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

From the experimental results gotten, the following conclusions can be drawn.

(1) It was observed that pH values of cassava mash reduced with an increase in retention time, the values tend towards the acidic region which shows that more cyanide would be leached out.

(2) The moisture content of cassava mash was also found to be close in range to the expected moisture content of cassava mash.

5.2 RECOMMENDATION

(1) Any rational process technology should ensure usage of raw materials (cassava) within 24 hours after harvest, this is done to avoid the rapid deterioration characteristic of cassava roots.

(2) The chemical Engineering Laboratory should be more equipped so that other students who want to carry out experiments on cassava would not go through too much trouble searching for equipments.

(3) Cassava has a wide range of use, it is a potential producer of ethanol, considering its potentially high yields and low cost. Therefore in view of the growing concern over the availability of cheap raw material, the ever increasing demand, the future of our fossil fuel and for the fact that life cannot be worthwhile without energy.

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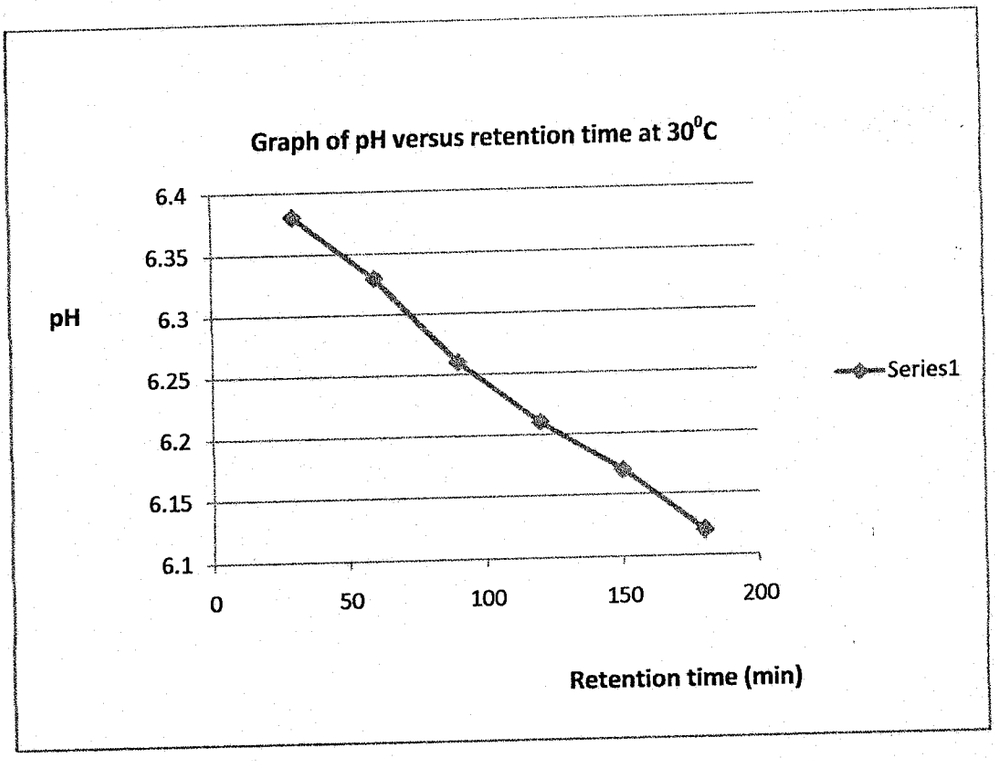
Graph of pH versus retention time at 30^{0}C
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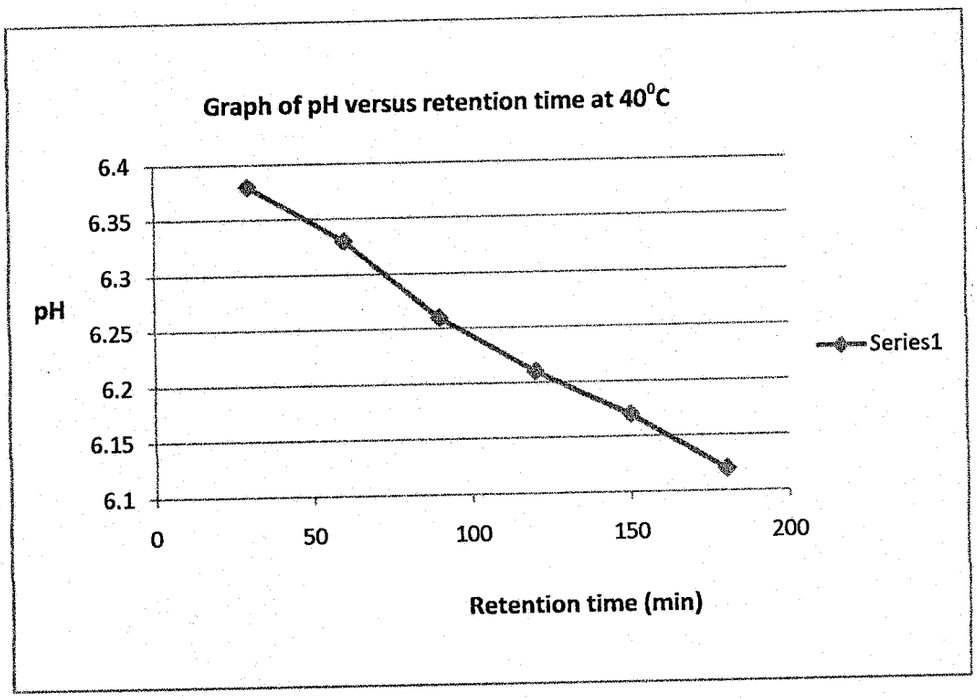
6.4
6.35
6.3
6.25
6.2
6.15
6.1
0
50
100
150
200
Retention time (min)
Series1


Graph of pH versus retention time at 40^{0}C
pH
6.4
6.35
6.3
6.25
6.2
6.15
6.1
0
50
100
150
200
Retention time (min)
Series1