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COMPARATIVE ANALYSIS OF GLUCOSE PRODUCED BY HYDROCHLORIC AND NITRIC ACIDS HYDROLYSIS OF UNRIPE PLANTAIN PEEL RESPECTIVELY

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Abstract: **In this research, the concentration of glucose produced by acid hydrolysis using hydrochloric and nitric acids respectively was determined and compared. The untreated unripe plantain peel was first characterized to determine its cellulose, hemi-cellulose, lignin, extractives and moisture contents; after which it was treated and characterized again. The characterization result revealed that on treatment, the cellulose content of the unripe plantain increased greatly; showing that glucose yield of the unripe plantain rose highly after treatment. The untreated and treated unripe plantain was analyzed using FTIR spectra techniques to determine the functional groups, which proved the existence of high amount of cellulose from which glucose can be produced. The yield of glucose in hydrochloric and nitric acid media by acid hydrolysis was also studied. The results revealed that while substrate dosage and acid concentration affected glucose yield in both acid media; however, maximum glucose yield was obtained at a substrate dosage of 1.5g in nitric acid whereas in hydrochloric acid medium, the glucose yield kept increasing after 1.5g substrate dosage. This meant that more glucose was obtained in hydrochloric acid medium than in nitric acid medium. The fatty acid methyl esters present in the glucose produced by acid hydrolysis was further analyzed using GC-MS techniques. This revealed that the glucose produced has desirable qualities for commercial use.**

Keywords: **Glucose, Unripe plantain peel, Biomass, Hydrochloric acid, Nitric acid.**

1. INTRODUCTION

Biomass is a collective term used for all materials that are biogenic in origin, i.e. derived from the product of photosynthesis. Biomass for energy use can be classified into industrial waste, landfill gas, agricultural crops and wastes, wooden biomass and alcohol fuels (Quaak and Knoef, 1999).The most abundant, readily available and renewable natural resource is lignocelluloses biomass ((Hsu et al., 2010; Ibrahim et al., 2011). Biomass wastes are also among the lignocelluloses materials that consist mainly of carbohydrate, extractives and ashes. Cellulose is the predominant component in lignocelluloses materials, followed by little quantity of hemicelluloses and lignin (Ibrahim et al., 2011; El-Zawawy et al., 2011). Cellulose is a biopolymer consisting of many glucose units connected through β-1,4-glycosidic bonds. The breakage of the β-1,4-glycosidic bonds by acids leads to the hydrolysis of cellulose polymers, resulting in the sugar molecule glucose or oligosaccharides (Kelly et al., 2014). It is already established that acid and enzyme hydrolysis are the two best ways for converting cellulose and lignocelluloses biomass to glucose and other monomeric sugars (Benkun, et al, 2009; Wu et al., 2010). Kumar et al., 2009 had opined that the keen interest in dilute acid hydrolysis is due to the fact that it is inexpensive and effective. Acid hydrolysis can be effectively carried out using either any of the following mineral acids: sulfuric acid, hydrochloric acid and nitric acid. The essence of this study is to determine and compare the concentration of glucose produced by acid hydrolysis of unripe plantain peel, using hydrochloric and nitric acids respectively.

2. MATERIALSAND METHODS

2.1 Materials:

Unripe plantain was purchased from Ikpoba hill market in Benin City Edo state. Ethanol (absolute), Sodium hydroxide (analytical grade), Acetic acid, Sulphuric acid, Hydrochloric acid, Nitric acid, distilled water. The equipment used are: beaker, measuring cylinder, electric digital weighing balance, heating mantle, soxhlet extractor, desiccator, water bath, oven, volumetric cylinder, conical flask, hot plate and stirrer, Petri dish, UV spectrometer, test tube, Isothermal shaker, Centrifuge, FTIR, Gas chromatography.

2.2 METHODS:

2.2.1 Substrate Preparation:

Unripe plantain was peeled. The peels were washed with water to remove all dirt particles and then sun dried for 8days. The washed peels were ground into fine particles using a grinding machine; after which they were stored in a polyethylene bag for further use.

2.2.2 Pretreatment of Biomass

Pretreatment of agricultural waste is necessary in order to remove lignin and hemicelluloses, reduce the crystallinity of cellulose, and increase the porosity of the lignocellulosic material. The alkaline treatment using sodium hydroxide was used following the method described by Muthurecayudham and Virthagiri (2010).20g of each sample were dissolved in 6w/v% NaOH, the solution was placed inside the water bath at 60ºC for 1hr and was washed with water till neutral pH was obtained and then dried in an oven at 105ºC until constant weight was obtained.

2.3 Separation of Cellulose from Unripe Plantain Biomass:

Layokun (1981) described the modified procedure for separation of cellulose from each sample of agricultural waste. The method involves addition of 20ml of diethyl ether to 10g of the powdered sample of unripe plantain peels in a 250 ml Erlenmeyer conical flask so as to remove the extractives. The resultant residue (free of extractives) was filtered and washed thoroughly with distilled water. 20 ml of 14M sulfuric acid was added to the washed residue in order to dissolve the cellulose and hemi-cellulose, leaving lignin as a hard precipitate, which was later filtered off. Cellulose was then obtained from the filtrate by adding 8M of sodium hydroxide solution to; thereby obtaining a residue that was predominantly cellulose; while hemi cellulose remained in solution. The solution was filtered and the resultant cellulose residue was then washed thoroughly with distilled water until a neutral pH was obtained. The cellulose residue was then dried at 80^{o}C in an oven until a constant weight was obtained for subsequent hydrolysis.

2.4 Acid Hydrolysis of Cellulose

5g of cellulose was added to 25ml of 0.5Mol/dm^3 hydrochloric acid and nitric acid in a 250ml conical flask, which served as a batch reactor and place in an isothermal shaker set at a temperature of 45ºC with an agitation speed of 150rpm and was allowed to operate for 4hrs and at intervals of 1hr, samples were withdrawn to determine the glucose concentration. The experiment was repeated at other temperature of 60, 75, 90, 105ºC and HCL and nitric acid concentration of 1.0, 1.5, 2.0 and 2.5mol/dm^3, respectively.

2.5 Determination OF Concentration of Glucose

The reducing sugar content (glucose) was determined by the DNS method with glucose as standard (Miller, 1959; Marsden et al., 1982). Absorbance was measured at 550nm. However, the DNS reagent was modified according to Mwesigye (1988). The dinitrosalicylic acid reagent for the determination of reducing sugar is composed of dinitrosalicylic acid, Rochelle salt, phenol and sodium hydroxide. 20g of potassium sodium tartarate (Rochelle salt) was dissolved in 20ml of distilled water in a beaker. 1g of sodium hydroxide was also dissolved separately in 20ml of water in a beaker. To the sodium hydroxide solution was added 1g of DNS and 0.3ml of phenol and stirred using a magnetic stirrer until the DNS was completely dissolved. The mixture was added to the 20g of potassium tartarate and stirred continuously until

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uniform mixture. The resultant solution was then made up to one litre distilled water. The mixture gave the stock of the modified DNS reagent containing 1%w/v DNS acid, 0.03% w/v phenol, 1% w/v sodium hydroxide and 20% w/v Rochelle salt (Mwesigye, 1988). The DNS reagent was then stored under refrigeration in an amber colored bottle.

3. RESULTS AND DISCUSSION

3.1.1 Characterization of treated and untreated unripe plantain peel

Table 1: Percentage composition of characterization of treated and untreated unripe plantain peel

Properties	Untreated Unripe Plantain Peel	Treated Unripe Plantain Peel
CELLULOSE	46.1	91.9
HEMICELLULOSE	45.7	40.5
LIGNIN	27.7	0.94
EXTRACTIVES	6.8	0.64
MOISTURE	2.5	2.8

This table shows the percentage composition of the constituents present in unripe, whether untreated or treated sample. It could easily be seen that cellulose and hemi-cellulose contents are highest in both treated and untreated samples. During treatment, the cellulose content increased from 46.1% to 91.9% (almost 100% increase), while the concentration of other constituents decreased. This implied that the treatment process carried out successfully altered the composition of the biomass by reducing the amount of the other constituents (Sun and Cheng, 2002).

3.2 Effect of substrate and acid concentrations on glucose yield from unripe plantain peel

3.2.1: Effect of substrate dosage on glucose concentration from unripe plantain peel

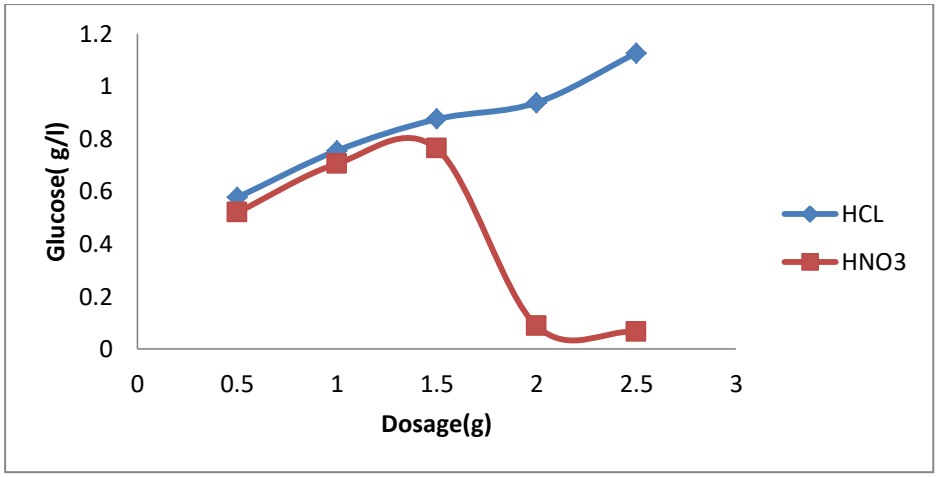

Fig 1: Effect of substrate dosage on the glucose concentration from unripe plantain peel.

Figure 1 expressed the relationship between glucose yield and substrate dosage using hydrochloric and nitric acid hydrolysis respectively. Initially, there was increase in the yield of glucose with increase in substrate dosage using HCl and HNO_3 acids for the acid hydrolysis respectively; but while the yield continued to increase with increased in substrate dosage in HCl medium, the glucose yield in HNO_3 medium started declining rapidly as the substrate dosage reached 1.5g and above. Thus, the yield of glucose in HNO_3 medium reached its optimum at a substrate dosage of 1.5g. In other words, the maximum amount of glucose produced in HNO_3 medium is significantly lesser than that produced in HCl medium. This decrease in glucose maybe attributed to the depletion of the acid.

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3.2.2: Effect of acid concentration on glucose yield from unripe plantain peel

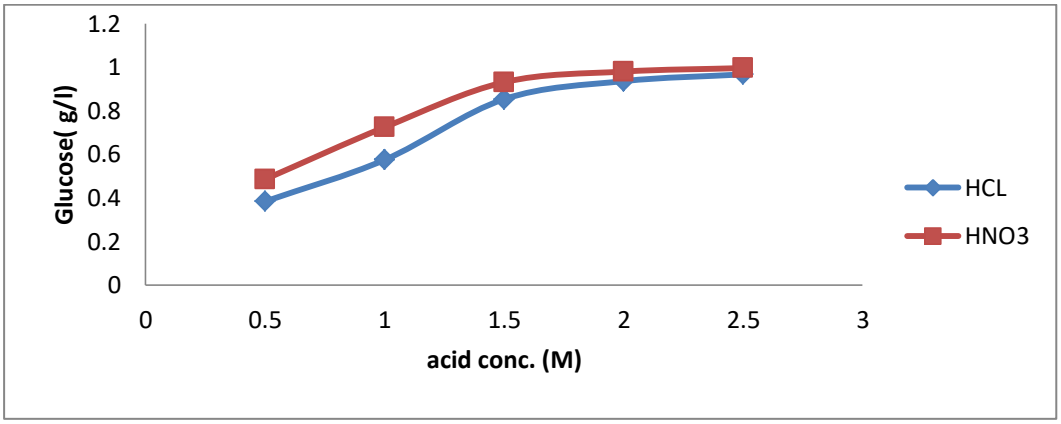

Fig 2: Effect of acid conc. on glucose yield from unripe plantain peel

Figure 2 shows the effect of acid concentration of glucose yield from unripe plantain peel. Generally, the concentration of glucose increased with the concentration of each acid; though there was slight decline in glucose yield as the acid concentration reached 2M and above. This could be attributed to the fact that at high acid concentration and relatively high temperature glucose can be converted to organic acid which led to decrease in cellulose concentration. Similar result was obtained by (Aberuagba, 1997).

3.3 Fourier Transform Infra-Red Spectroscopy (FTIR)

3.3.1 FTIR spectra of untreated plantain peel

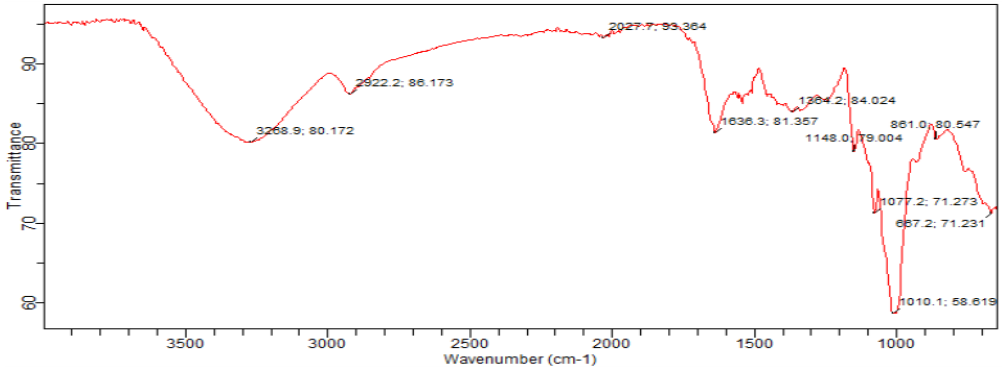

Fig 3: FTIR spectral analysis of developed sample of untreated plantain peel.

3.3.2 FTIR spectra of treated plantain peel

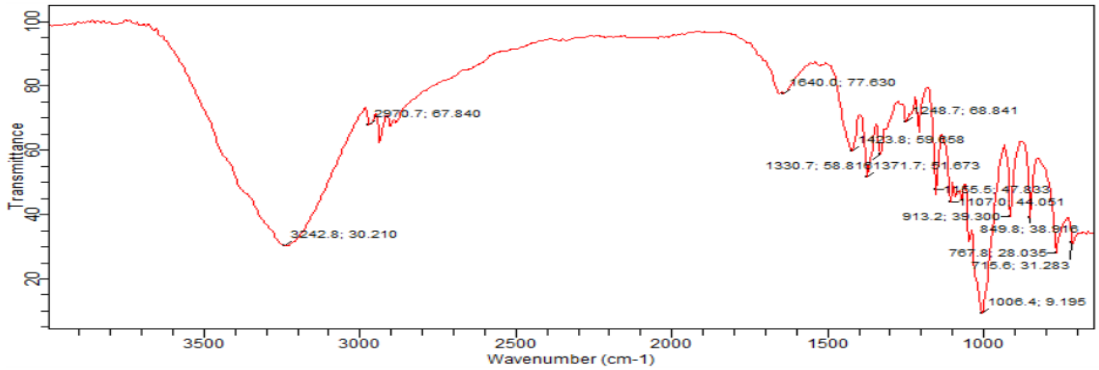

Fig 4: FTIR spectral analysis of developed sample of Treated plantain peel

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According to the FTIR spectrum, the wave number increased from 667.2-3268.9 (cm^{-1}) for untreated plantain peel and from 715.6- 3242.8 for treated plantain peel. In untreated plantain peel, the peak around 667.2cm^{-1} (C-Br stretch) shifted to higher frequency 3268.9cm^{-1} (N-H stretch), while the peak around 715.6cm^{-1} for treated plantain peel (C-H rock) shifted to higher frequency of 3242.8cm^{-1} (N-H stretch). The shifts in peaks and intensities of the functional groups can be attributed to reduction in the amount of lignin and hemicelluloses and increase in the porosity of the lignocellulosic material after treatment.

GC-MS ANALYSIS OF THE PRODUCED GLUCOSE

The fatty acid methyl ester (FAME) present in the glucose produced from unripe plantain peels was determined using Gas chromatography-mass spectrometry (GC-MS). This is necessary to identify the compounds present in the glucose produced from treated unripe plantain peels by acid hydrolysis.

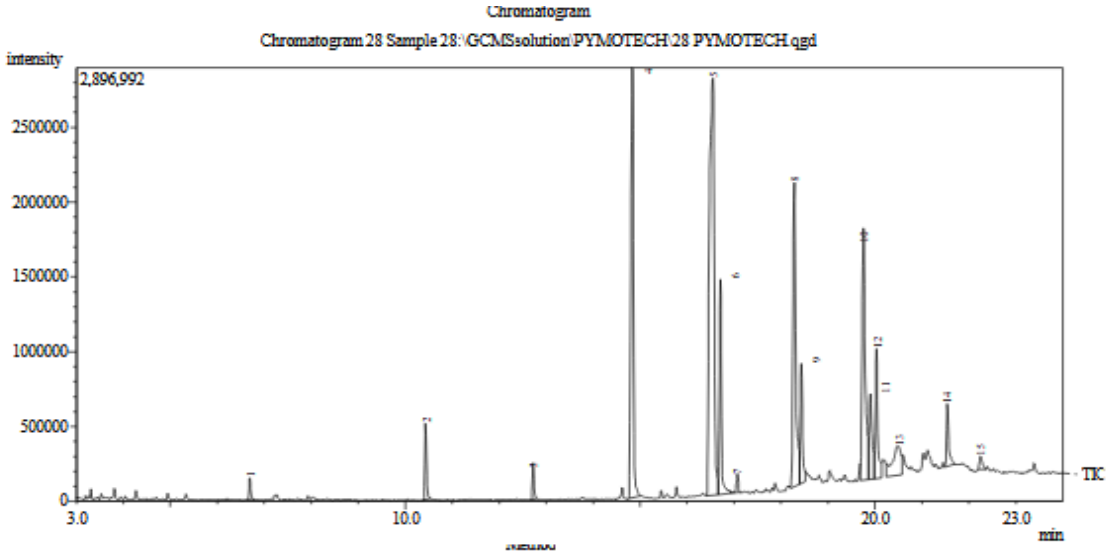

Fig 4.1: GC-MS of produced glucose.

Table 2: The results from the gas chromatography analysis of glucose produced from unripe plantain peel.

Name of Compounds	Molecular Formula	Molecular Weight	Retention Time (min)	Retention Index
Octanal	$C_{10}H_{22}O_2$	174	6.690	998
Duodecanoic acid	$C_{13}H_{26}O_2$	214	10.433	1481
Pentadecanoic acid	$C_{17}H_{34}O_2$	270	12.724	1814
Tridecanoic acid	$C_{14}H_{28}O_2$	228	14.837	1580
Octadecenoic acid	$C_{19}H_{36}O_2$	296	16.547	2085
Hexadecanoic acid	$C_{18}H_{36}O_2$	284	16.710	1914
Hexadecenoic acid	$C_{18}H_{34}O_2$	282	17.073	1986
Glycerol 1,2-dipalmitate	$C_{35}H_{68}O_5$	568	18.283	4013
Eicosanoic acid	$3C_{21}H_{42}O_2$	326	18.433	2276
Tridecanol	$C_{13}H_{28}O$	200	19.758	1556
Pentadecanoate	$C_{18}H_{34}O_2$	316	19.905	2399
Ducosanoic acid	$C_{23}H_{46}O_2$	354	20.033	2475
Hexadecenal	$C_{17}H_{32}O$	252	20.483	1843
Tetracosanoic acid	$C_{25}H_{50}O_2$	382	21.542	2674
Allyl hexanoate	$C_9H_{16}O_2$	156	22.243	1073

Table 2 revealed the alkanols, alkanoic acids and esters present in the glucose. The table also showed that the glucose produced is a strong reducing agent because of the presence of the –CHO- group.

4. CONCLUSIONS

The high cellulose content of raw (untreated) unripe plantain indicated that it has high potential to yield significant amount of glucose. The large increase in the quantity of cellulose after the treatment of the unripe plantain indicated that the pre-treatment process was a positive and an effective way of increasing the glucose yield. The relationship between glucose yield and substrate dosage as well between glucose yield and acid concentration showed that more glucose was produced when the acid hydrolysis was carried out using hydrochloric acid; which implied that hydrochloric acid is more effective than nitric acid in carrying out the glucose production acid hydrolysis. The GC-MS result showed that glucose produced has desirable properties for commercial demands.

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