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ACID HYDROLYSIS OF YAM PEELS AND HYDROLYSATE BIOCHEMICAL PROFILING: PROCESS KINETICS AND THERMODYNAMICS STUDIES

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ABSTRACT

Yam peel (YP) was hydrolyzed using sulphuric acid at concentrations of 0.5, 1.0, and 1.5 M and temperatures of 70, 90, and 110oC for glucose syrup (GS) production. The kinetics and thermodynamics of the hydrolysis were investigated to check the statistical consistency of the process. The hydrolysate obtained as GS was characterized for its biochemical compositions. An ideal rate constant (k) of 0.07 was obtained at a temperature of 110oC and an acid concentration of 1.5 M, resulting in the highest GS of 46.44 g/l from a YP concentration of 50 g/l. The ANOVA findings showed that the acid concentrations and temperatures had a significant impact on the hydrolysis, with F > F critical (F critical = 18.51282) and a probability of <0.05. The greatest value of ΔH was 27.7 x 103 Jmol-1 at 1.5 M and 70oC, and the lowest value of ΔS was −7.24 x 10 Jmol-1 at 1.5 M and 110oC, according to the thermodynamic analysis. The ΔG values rose with temperature and acid concentration from 5.15 x 104 to 5.51 x 104 Jmol-1. Based on these thermodynamic parameters, the GS produced is stable. The existence of flavonoids, alkaloids, phenols, tannins, glycosides, steroids, and saponins, in the hydrolysate justifies it as a worthy substrate for pharmaceutical products. Therefore, hydrolysis of YP presents a potential approach that lowers the cost of producing GS and provides a suitable substrate for the production of beverages and food items.

Keywords: *Yam peels, hydrolysis, kinetics, thermodynamic, activation energy, and glucose syrup.*

1.0 INTRODUCTION

Yams are constituents of the Dioscoreaceae family, which has roughly 650 species. The most significant genus has roughly 600 species and is called Dioscorea. Only seven of them are major sources of food for humans in the tropics (Wanasundera & Ravindran, 1994). Nigeria is the world's largest producer of yams, producing between 70 and 76 percent of global yam production. According to Food and Agricultural Organization research, Nigeria produced 18.3 million tonnes of yam from 1.5 million hectares in 1985, making up 73.8% of all yam production in Africa. The tuber is the essential component of a yam plant, which is an excellent source of energy due to its substantial amount of carbohydrates with low protein and lipid composition. Although yam being a starchy tuber is mainly used in food preparation, it has found potential applications in other fields such as pharmaceutical, beverages, and bioplastic production (Villadiego-del Villar et al., 2021). This is because of its natural composition which includes: starch (21%), fat (1%), water (36%), protein (13%), mineral matter (2.5%), and albuminoids (10%) (Hashimi, 2021). In another research work, yam was reported to typically contain an average of 7.4% crude protein, with the remainder of the dry matter between 75.6 and 84.3% belonging to carbohydrates (Wanasundera & Ravindran, 2014). These research findings confirmed that tubers of yam are highly rich in carbohydrates which is a candidate for glucose production.

Tubers such as yam can be processed as a feedstock to produce alternative sugar and sugar syrup. The tubers' starch content is extracted and processed through hydrolysis to alternative sugars (Wahyusi et al., 2022). However, continuous use of yam tuber as a feedstock for alternative sugars would compete with food. This would create challenges for food security and food industries, hence the need for alternative feedstocks for sugar syrup production (Omoruyi et al., 2022). Agricultural residues such as yam peel for sugar syrup production and other products such as biobutanol could be an economically feasible and eco-friendly alternative feedstock (Jin et al., 2022). This is due to their huge energy potential as they contain the much-needed starch component that can undergo hydrolysis to produce glucose (C6-sugar) (Omoruyi et al., 2022). The starch polymers in the peel are broken down into sugar molecules with shorter chains through the hydrolysis process (Wahyusi et al., 2022). Fermentable sugars such as oligosaccharides, disaccharides, mono-saccharides, and polyols which are composed of short chains of sugar molecules are the products of hydrolysis (Bethel-Wali et al., 2023).

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The hydrolysis process could either be enzymatic hydrolysis or acid-catalyzed hydrolysis (Omoruyi et al., 2022). However, acid hydrolysis proffers the advantage of taking a shorter reaction time compared to enzyme hydrolysis (Yusuf et al., 2020). Also, acid hydrolysis is a common chemical method in the industrial processing of starch, which is relatively simple (Zhang et al., 2023). The process is an important chemical modification that could expressively change the structural and functional properties of starch without disrupting its granular morphology (Okunlola & Lawal, 2022). In the hydrolysis process, acid as a catalyst reacts and de-polymerizes the amorphous regions of the starch granules to yield glucose syrup. The degree of the hydrolysis process is then determined by the dextrose equivalent of the crude maltose solution (Purwadi et al., 2021). Meanwhile, the yield of glucose syrup through acid hydrolysis was reported to depend on the acid concentration, reaction time, and temperature (Okunlola & Lawal, 2022). Hence, the need to investigate the effects of acid concentration, and temperature over reaction time in this work.

An essential aspect of the response that needs to be studied for the synthesis of D-glucose is the kinetic and thermodynamic parameters that characterize the hydrolysis reaction (Gurgel et al., 2012). Kinetic models for the hydrolysis of lignocellulosic materials illustrate the relationship between the main state variables and also describe the process of hydrolysis in terms of quantity (Hodge et al., 2008; Lin & Tanaka, 2006)). To successfully transform agricultural wastes such as yam peel into usable products, it is imperative to find the kinetic model that accurately explains the hydrolysis process (Agler et al., 2011; Onyelucheya et al., 2016). The model should be based on the breakdown of long chains of hemicellulose to form shorter oligomers because between 50 and 90% of the cellulose in lignocellulose is bonded by hydrogen bonds with a crystalline structure (Jacobsen & Wyman, 2000).

The continuous breakdown of the hydrogen bonds leads to the production of monomeric sugars. For any process where the rate of reaction is catalyst and temperature-dependent, thermodynamic factors are crucial to assess the magnitude of the reaction and its equilibrium state (Sarma, Dolui, & Kumar, 2014). Hence, it is important to investigate the kinetic and thermodynamic aspects of the acid hydrolysis of yam peel by evaluating some parameters such as; Activation energy (Ea), Arrhenius factor (A), Standard enthalpy change (H), Gibbs free energy (Go), Standard entropy change (S), and Equilibrium constant (K) (Rinaldi & Schüth, 2009).

This study aimed to investigate the effects of acid concentrations and temperatures over time on the glucose syrup concentration recovery from yam peel through acid hydrolysis. The results of the hydrolysis were subjected to kinetics and thermodynamic models while the data obtained from the models were tested for their statistical consistency. The glucose syrup was characterized for its phytochemical properties using a Gas Chromatography-Mass Spectrum (GC-MS) and Fourier Transform Infrared Spectrum (FTIR).

2.0 MATERIALS AND METHODS

2.1 Materials

Yam peel was collected from a yam flour processing factory in Gambari, Ogbomoso, Oyo State, Nigeria. An Atomic Absorption Spectrophotometer (AAS) and Flame Photometer (FP) Buck Scientific Accusys 211, equipped with air-acetylene for the flame, was used for elemental characterization of the yam peel. All chemicals used were of analytical grade and purchased from Sigma-Aldrich.

2.2 Preparation of Yam Peel Sample

The collected yam peel was carefully separated from undesirous substances by hand picking and was washed thoroughly with distilled water to get rid of sand and other debris on the material. The washed peel was shredded into small pieces of 1 to 2 cm sizes with the aid of a stainless-steel knife. It was sun-dried for three days and then oven-dried at 70°C until constant weight was attained. The yam peel sample was ground to powder using a grinding machine and screened to <100 µm diameter. The powder sample was packed into a sealable plastic bag and stored in desiccators for further use.

2.3 Chemical Characterisation of Yam Peel

The modified method of Ajala et al. (2018) was followed by digesting the yam peel using the aqua regia (HNO_3 67%: HCl 37% = 3:1) method. A calibrated microwave oven (Berghof MWS-2) with six closed PFA 100 ml high-pressure vessels was employed for the digestion. The digested sample was characterized for carbohydrate, crude protein, crude fat, moisture, and ash contents using the AOAC standard methods (Aletan & Kwazo 2019). The AAS/Flame Photometer was used to determine the concentrations of sodium (Na), potassium (K), iron (Fe), calcium (Ca), and magnesium (Mg) in the sample. The absorbance and concentration of the metals were measured by direct aspiration into the burner using the wavenumber corresponding to each element as provided by the manufacturer.

2.4 Acid Hydrolysis of Yam Peel

The modified approach reported by Gaewchingduang and Pengthemkeerati (2010) was taken into consideration for the hydrolysis. Sulphuric acid (H_2SO_4) in varied doses of 0.5, 1.0, and 1.5 M was used for the hydrolysis of yam peel. A 250 ml Erlenmeyer conical flask was filled with 100 ml of the acid solution and 5 g of the yam peel sample. The mixture in the flask was heated for 120 minutes at temperatures of 70, 90, or 110°C using a magnetic stirrer. Ten milliliters (10 ml) of the sample was withdrawn at intervals of 20 min of the experiment and centrifuged at 3,000 rpm for 10 min. Three milliliters (3 ml)

of the supernatant was collected for the DNS assay analysis to ascertain the reducing sugar concentration.

2.5 Statistical Analysis

The data obtained from the proximate analysis were evaluated for mathematical consistency using IBM SPSS Statistics 19, and the results were the mean of three replicates. The Analysis of variance (ANOVA) on the effects of acid concentrations and temperatures on the GSC was studied using the statistical package of Microsoft EXCEL 2016. The analysis was considered statistically significant at the 5% level ($p \leq 0.05$).

2.6 Analysis of the Glucose Syrup Concentration (GSC)

The adapted procedure of Miller (1959) was followed to prepare the 3, 5 – dinitro salicylic acid (DNS) assay solution and to also determine the glucose syrup concentration (GSC). To make the DNS test solution, 10 g of pellet NaOH was dissolved in 200 mL of distilled water. Ten grams (10 g) of 3, 5 - dinitro salicylic acid, 0.5 g of sodium bisulfite, 2.52 ml of 80% phenol, and 200 g of Rochelle salt were added to the initial solution of NaOH and stirred to dissolve. The solution was made up to 1 L with distilled water and thoroughly mixed until it dissolved. The DNS assay solution was preserved in a 2 L Amber bottle and kept inside a refrigerator at 4^{o}C. The withdrawn sample of hydrolysate was tested for its concentration using the DNS solution in the UV spectrophotometer at a wavelength of 540 nm. Then, the Dextrose Equivalent was evaluated and expressed in percentage (or percentage substrate conversion) based on Equation 1:

$$DE = \frac{\text{Reducing sugar expressed as glucose (g/l)}}{\text{Total carbohydrate (g/l)}} \quad 1$$



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Equation 4 was considered the basic equation for developing a kinetic model that best reflects the acid hydrolysis of lignocellulose material for glucose syrup recovery. Thereafter, the flowing assumptions were made to develop the model:

- Cellulose and hemicellulose were regarded as reactant units.
- Slow hemicellulose was used to describe the reaction.
- Formation of oligomers is vital to describe the performance of the hydrolysis.
- The glucose recovered was not allowed to degrade to furfuryl and other inhibitory by-products but rather the reaction was truncated once it reached maximum glucose recovery.
- The reaction was taking a first-order reaction.

Hence, a modified Equation 4 was considered best to develop the model which is given in Equation 5:



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Where; k_1 and k_2 are the reaction rate constants for the two reaction steps.

The reaction mechanism depicted in Equations 6–8 was applied to build the model equation which represents the acid-hydrolysis of yam peel by fitting data from experiments to estimate the kinetic parameters.

2.7 Testing of Kinetic Model and Thermodynamics Analysis

2.7.1 Kinetic model

A kinetic model was developed and reported by Ajala et al. (2020) for the acid hydrolysis of cassava peel which was adapted for this study. Equation 2 gives the general expression for the hydrolysis of hemicellulosic material which yields hexose sugars (glucose, galactose, and mannose) (Mukherjee et al., 2017).

$$(C_6H_{10}O_5)_n + nH_2O \longrightarrow nC_6H_{12}O_6 \quad 2$$

Whereas, Equation 3 can be used to show the stoichiometry that results from the addition of water to pentose sugar molecules during hemicellulose hydrolysis.

$$(C_5H_8O_4)_n + nH_2O \longrightarrow C_5H_{10}O_5 \quad 3$$

However, it was proposed that dilute-acid cellulose and hemicellulose hydrolysis could proceed according to a kinetic model predicated on the first-order expression, for reactants with an Arrhenius temperature dependence and an acid concentration raised to a power. Then, the technique was shown to be inadequate because it portrays the reaction as homogenous rather than heterogeneous. This suggests that more research is needed to fully comprehend the fundamental basis of biomass hydrolysis. Therefore, a modified approach of Jacobsen and Wyman (2000) that best described the hydrolysis of hemicellulose by having two fractions breaking down into sugars was considered and given in Equation 4:

$$\frac{d[Cp]}{dt} = k_1[Cp] \quad 6$$

$$\frac{d[O]}{dt} = k_1[Cp] - k_2[O] \quad 7$$

$$C_{Cpo} = C_{Cp} + C_O + C_G \quad 8$$

Resolving the Differential Equations 6 and 7 with appropriate boundary conditions resulted in Equations 9 – 11 respectively.

$$C_{Cp} = C_{Cpo}e^{-k_1 t} \quad 9$$

$$C_o = k_1 C_{po}\left[\frac{e^{-k_1 t}}{k_2 - k_1} + \frac{e^{-k_2 t}}{k_1 - k_2}\right] \quad 10$$

$$C_G = C_{Cpo}\left[1 + \left(\frac{k_2}{k_1 - k_2}\right)e^{-k_1 t} + \left(\frac{k_1}{k_2 - k_1}\right)e^{-k_2 t}\right] \quad 11$$

Based on the assumption made Equation 11 becomes

$$C_G = C_{Cpo}\left(1 - e^{-k_2 t}\right) \quad 12$$

In order words, the rate is dictated by the second step of a two-step reaction that is governed by k_2, thus, the step that moves slowly has the biggest impact on the entire reaction rate.
Linearizing Equation 12 gave Equation 13;

$$\ln\left[1 - \frac{C_G}{C_{Cpo}}\right] = -k_2 t \quad 13$$

Where, $Y = \ln\left[1 - \frac{C_G}{C_{Cpo}}\right]$ and X = t when an intercept is 0.
As a result, slope = k_2,
when Y is plotted against X in a straight-line graph and as such is the rate constant of the reaction.

2.7.2 Thermodynamic study

Thermodynamic parameters are critical in defining the extent of the reaction and the state of equilibrium in any catalyzed reaction process. Whenever metabolic control analysis is also needed for any reaction, both the thermodynamic and kinetic parameters play significant roles (Sarma et al., 2014; Stumm & Morgan, 2012). Therefore, the models according to Kouamé et al. 2017) and Sarma et al. (2014) were considered to calculate the energy of activation (Ea), Arrhenius factor (A), standard enthalpy change (∆H), standard entropy change (∆S), and Gibbs free energy (∆G) for sulphuric acid-catalyzed hydrolysis reaction of yam peel. The models are as presented in Equations 14 to 17:

$$k = Ae^{-E_a/RT} \quad 14$$

The linearization of Arrhenius Equation (14) and plotting $\ln k$ against 1/T yielded the activation energy (E_a), and Arrhenius factor (A) values. The obtained values of the E_a and A were used to determine the different thermodynamic values of ∆H, ∆S, and ∆G using Equations 15, 16, and 17 respectively.

$$\Delta H = E_a - RT \quad 15$$

$$\Delta S = R\,(\ln A - \ln K_B)/(h_p - \ln R) \quad 16$$

$$\Delta G = \Delta H - T\Delta S \quad 17$$

Where; Boltzmann's constant (K_B) is equal to 1.38 x 10^{-23} J.K^{-1}, The Planck's constant (h_p) is equal to 6.626 x 10^{-34} J.s and the gas constant (R) is equal to 8.314 J.mol^{-1}. K^{-1}.

2.8 Phytochemical Profiling of Yam Peel Hydrolysate

2.8.1 Phytochemical characterization

The phytochemical properties of the hydrolysate were analyzed using standard procedures described by Doughari & Saa-Aondo (2021); Willie et al. (2021) and Olaniyan & Ajayi (2021). The chemical compounds investigated in the hydrolysate are alkaloid, phenol, tannin, flavonoid, glycoside, saponin, and steroid.

2.8.2 Characterization of bioactive chemicals in the hydrolysate through GC-MS

Analysis of the GC-MS for the yam peel hydrolysate followed the procedure reported by Ajala et al. (2020). It was carried out by an Agilent GC (7890A) hyphenated to a mass spectrophotometer (MS) (5975C). The GC-MS used possesses a triple-axis spectrometer with an auto-injector of 10 µl syringe which employs helium as an injection gas. All chromatographic separations were carried out on a capillary column with dimensions of 30 m length 0.2 m internal diameter 250 m thickness and was treated with phenyl methyl siloxane. The operational parameters for the GC-MC are as follows: an ion source temperature (EI) of 250°C, an interface temperature of 300°C, a pressure of 16.2 psi, an out time of 1.8 min, a split ratio of 1:50, a 1 µl injector in split mode, and an injection temperature of 300°C. The column temperature increased by 4°C/min from 35°C to 150°C after starting at 35°C for 5 min. At a rate of 20°C/min, the temperature was raised to 250°C and maintained there for 5 min. The entire elution took 47.5 min to complete. The chemical components were identified by comparing the mass spectra obtained with those of the standard mass spectra from the NIST Library (NISTII) (Belakhdar et al., 2015).

2.8.3 Functional groups in the hydrolysate through FTIR

An FTIR (NICOLET iS5, Thermo Scientific) was used to measure the infrared spectra of the yam peel hydrolysate in the region of 4000-400 cm^{-1}. The purpose of the investigation was to identify the major functional groups present in the hydrolysate. The hydrolysate was added with potassium bromide crystals, put in the KBr cells, and then placed into the spectrophotometer's sample compartment. The spectra were displayed as % transmittance versus wavenumbers.

3.0 RESULTS AND DISCUSSION

3.1 Chemical Characterization of Yam Peel

Table 1(a and b) shows the proximate and elemental compositions of the yam peel, respectively. It was observed that carbohydrate (76.20 ± 0.007%) was found to be the most abundant component, followed by moisture content (10.85 ± 0.014%) and ash content (4.63 ± 0.007%) for the proximate analysis. Other components, such as crude protein (3.67 ± 0.014%), lipid (1.44 ± 0.014%), and fiber content (3.22 ±

0.014%) are present, but in low quantity. Since there is over 70% by weight of carbohydrates in the yam peel hydrolysate, it is a potential carbon source for metabolic processes (Sebayang et al., 2017). The results obtained from the elemental analysis show Na of 4.68 mg/L, K of 440 mg/L, Fe of 0.1 mg/L, Ca of 1.8 mg/L, and Mg of 3.09 mg/L. The hydrolysate has significant minerals in abundance, as well as nutritional compositions based on the findings of this study, and as such can be useful in the development of new drugs, yeast growth, and enhanced ethanol fermentation (Ahongshangbam & Shantibala, 2017; Moshi et al., 2015). Furthermore, yam peel hydrolysate can also be an ideal substrate for biotechnological processes to produce metabolites (Woiciechowski et al., 2002).

Table 1a: Proximate Analysis of Yam Peel Sample

Proximate	Percentage composition
Carbohydrate content	76.20 ± 0.007
Moisture content	10.85 ± 0.014
Ash content	4.63 ± 0.007
Crude protein	3.67 ± 0.014
Lipid	1.44 ± 0.014
Fibre content	3.22 ± 0.014

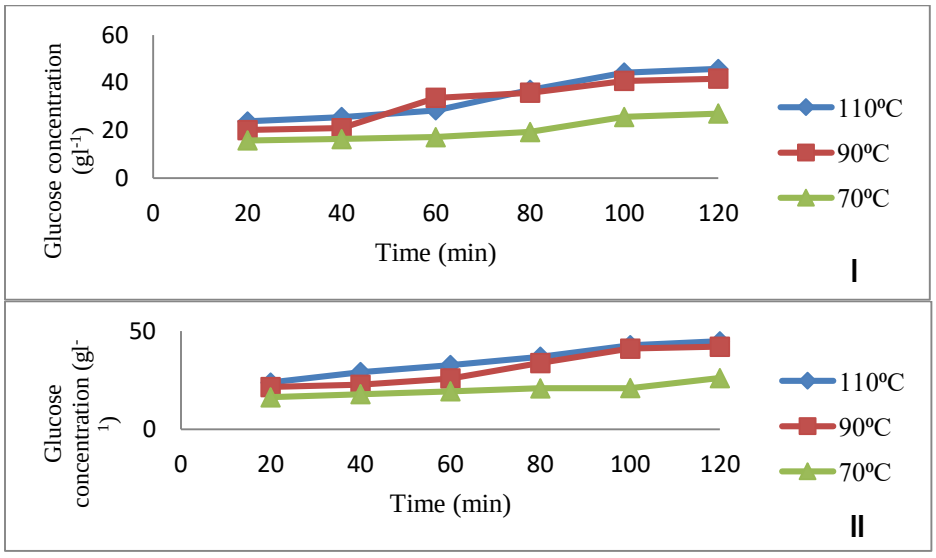
Table 1b: Elemental Composition of Yam Peel Sample

Elements	mg/L
Na	4.68
K	440
Fe	0.1
Ca	1.8
Mg	3.09

3.2 Acid Hydrolysis of the Yam Peel

The glucose syrup concentration (GSC) obtained over a period using various temperatures of 70, 90, or 110°C at varied concentrations of H_2SO_4 at (I) 0.5 M, (II) 1.0 M, or (III) 1.5 M is shown in Figure 1. It was observed that the GSC increased steadily for the first 80 min and reached a plateau at 120 min with no further increase. At 0.5 M (Case I), the GSC grew consistently for 100 min, which was an exception. For the various concentrations of H_2SO_4, the maximum GSC recovered was 44.787, 45.78, and 46.44 g/l, for Cases I, II, and III, respectively at 110°C. The next highest GSC recovery was at 90°C, while the lowest GSC recovery was at 70°C.

The efficiency of yam peel hydrolysis improved as the temperature rose from 70°C to 110°C. The result's trend is consistent with those of other methods of cellulose hydrolysis reported in the literature (Chen et al., 2018; Kupiainen et al., 2014). The finding is a validation of the fact that an increase in hydrolysis temperature positively favored the GSC yield; as it agreed with results obtained in the previous work of Ajala (2020). The increase in temperature brings more frequent collision between molecules so the GSC formation increases. More so that the long-chain cellulose molecules would break easily to form glucose monomers (Egbosiuba et al., 2014; Muhaimin & Sri, 2017). The GSC recovered over time at the different H_2SO_4 concentrations and the temperatures reported are shown in Figure 2..



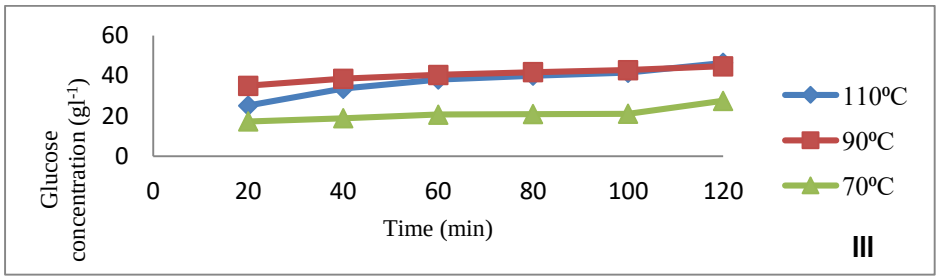


Figure 1: GSC over time at different temperatures and acid concentrations of (I) 0.5, (II) 1.0, and (III) 1.5 M

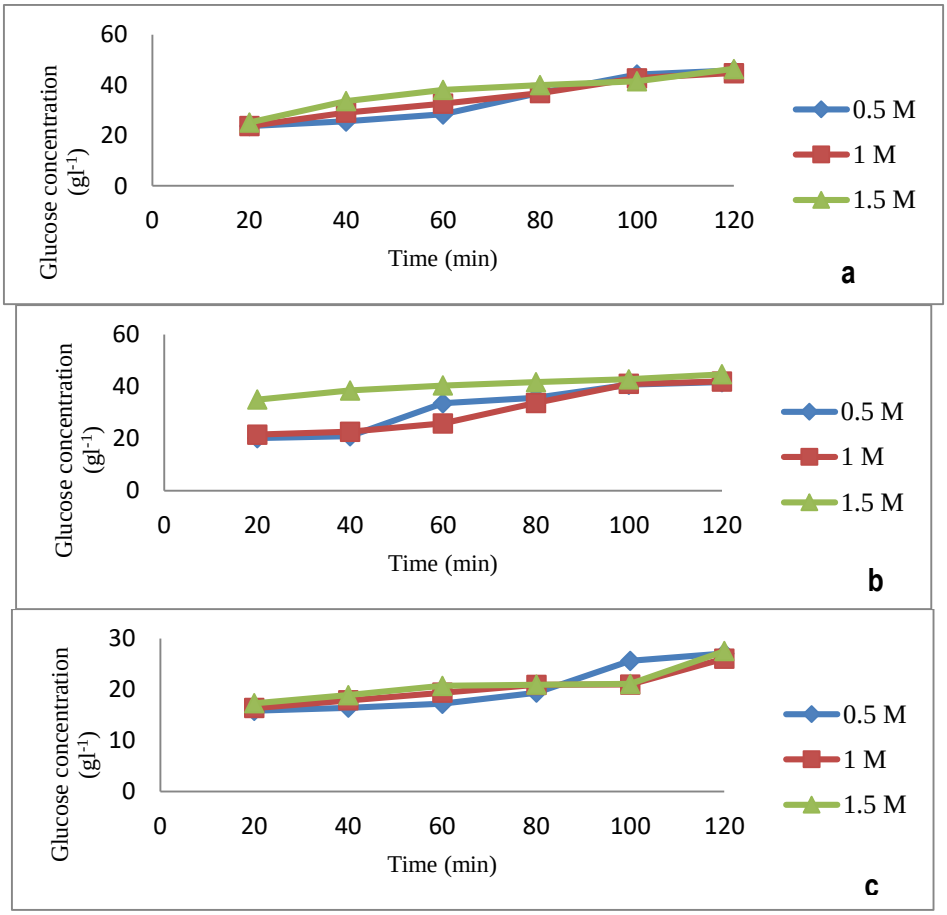


Figure 2: GSC over time at different acid concentrations and temperatures of (a) 70, (b) 90, and (c) 110ºC

It was observed from the figure that the increase of GSC from 1.0 M to 1.5 M of acid concentration yielded a marginal increase. The marginal increase might be due to the dehydrating effect of higher acid concentration on yam hydrolysis (Egbosiuba et al., 2014; Kargarzadeh et al., 2012; Lenihan et al., 2010). The pattern of this result is similar to the observation of Onyelucheya et al. (2017).

The ANOVA was examined to evaluate the relationship that exists among the three groups of acid concentrations (0.5, 1.0, and 1.5 M) and temperatures (70, 90, and 110ºC) on the hydrolysis of yam peel. The results are shown in Table 2. At constant temperature conditions and varying acid concentrations; (0.5, 1.0 and 1.5 M) 70ºC, (0.5, 1.0 and 1.5 M) 90ºC and (0.5, 1.0 and 1.5 M) 110ºC, the ANOVA results of F > F critical (F crit = 18.51282) and p<0.05 are 5893.99 and 0.00017, 883.4919 and 0.00113, and 11741.07 and 8.52E-05, respectively. The results propose that there is a substantial difference between the means of the group of acid concentrations at the constant temperature; an affirmation of the fact that the effect of acid concentrations on the hydrolysis is significant. Similarly, the ANOVA results of F > F crit (F crit

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= 18.51282) and p<0.05 for various temperatures at constant acid concentration; (70, 90 and 110°C) 0.5 M, (70, 90 and 110°C) 1.0 M and (70, 90 and 110°C) 1.5 M are 31.46179 and 0.030345, 30.3972 and 0.031359, and 29.38329 and 0.032389, respectively. These results also indicate that there is a significant difference between the means of the group of temperatures at constant acid concentration; thus, signifying that the effect of temperatures on the hydrolysis is significant. Based on this analysis, it could be established that both acid concentration and temperature strongly enhanced the yam peel hydrolysis (Zhao et al., 2008).

Table 2: ANOVA on Effects of Acid Concentrations and Temperatures

Variable Parameters	Constant Parameters		SS	Df	MS	F	P-value
Acid concentrations of 0.5, 1.0, and 1.5 M	Temperatures (C)	70	0.2308	2	0.1154	5893.99	0.00017
		90	4.01705	2	2.008525	883.4919	0.00113
		110	0.3428	2	0.1714	11741.07	8.52E-05
Temperatures of 70, 90 and 110°C	Acid concentrations (M)	0.5	204.7032	2	102.3516	31.46179	0.030345
		1.0	207.22	2	103.61	30.3972	0.031359
		1.5	201.3945	2	100.6972	29.38329	0.032389

*F crit. = 18.51282

3.3 Kinetics Analysis

The results of the rate of glucose production with a rate constant (k), the coefficient of regression (R^2), and the adjusted coefficient of regression (adj. R^2) are presented in Table 3. The results were obtained by fitting the experimental data into a first-order kinetic model of Eq. 13 (Ajala et al., 2018) as shown in Figure 3 (i - iii). The rate constant obtained for 0.5 M acid concentration at temperatures of 70, 90 and 110°C is 0.007, 0.0161, and 0.0196, respectively with R^2 and adj. R^2 being 0.866 and 0.832, 0.954 and 0.943, and 0.908 and 0.885, respectively.

The values obtained for 1.0 M acid concentration at temperatures of 70, 90, and 110°C are 0.0066, 0.0154, and 0.0188, respectively with R^2 and adj. R^2 as 0.865 and 0.831, 0.912 and 0.890, and 0.961 and 0.950, respectively. The k values that were obtained for 1.5 M acid concentration at temperatures of 70. 90 and 110°C are 0.07, 0.0218, and 0.0211, respectively with R^2 and adj. R^2 as 0.752 and 0.690, 0.987 and 0.973, and 0.927 and 0.908, respectively. The rate of glucose production was seen to increase with an increase in acid concentration and with an increase in temperature. Hence, the highest rate of reaction was achieved at an acid concentration of 1.5 M and temperature of 110°C with a k value of 0.07.

The results of the model showed good fits and adequate prediction due to the obtained R^2 and adj. R^2 values which fall within a range of 0.690 and 0.987. These indicate that between 69.0% and 98.7% of the experimental data were significant and the model did not explain only between 31.0% and 1.3% of the total variations. Since R^2 and adj. R^2 obtained in this study gave the best values from about 70%, so it can be theoretically concluded that the hydrolysis of yam peel fit the first-order reaction. The outcomes of this study agree with the values reported by Onyelucheya et al. (2016), Xiang et al. (2003), and Jiang et al. (2010). Liu et al. (2012) also observed a comparable rate constant of k_f = 0.0311 min^{-1}, k_s = 0.0026 $min^{-1,}$ and k_2 = 0.0069 min^{-1} for the hemicellulose hydrolysis of sweet sorghum bagasse at 120°C.

3.4 Thermodynamic Analysis

Figure 4 shows the Arrhenius plot of the acid concentration at different temperatures which was employed to evaluate the activation energy (Ea) and the frequency factor (A) for yam peel hydrolysis. The Ea, ΔG^o, ΔH, and ΔS for acid concentration at different temperatures were computed using the equations above with the results presented in Table 4(a and b). The Ea and A were found to be 28100 $Jmol^{-1}$ and 145.42, 28500 $Jmol^{-1}$ and 161.9, and 30500 $Jmol^{-1}$ and 369.52 for 0.5, 1.0, and 1.5 M concentrations of H_2SO_4, respectively. These values are comparable with activation energies of 50.54 kJ/mol, 50.78 kJ/mol, and 50.40 kJ/mol reported by Kralj (2007). The Ea obtained in this study is high, which is indicative of the natural hydrolysis of yam peel. However, the least of Ea is that of 0.5 M which further showed that the acid concentration significantly affects the hydrolysis.

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Table 3: Determination of Rate Constant (k) using a First Order Kinetic Model

Process Conditions Acid (M)	Temp. (C)	SS	R^2	Adj. R^2	Slope (k)	SE
0.5	70	0.020	0.866	0.832	0.007	0.071
	90	0.068	0.954	0.943	0.0161	0.130
	110	0.282	0.908	0.885	0.0196	0.266
1.0	70	0.009	0.865	0.831	0.0066	0.049
	90	0.014	0.912	0.890	0.0154	0.187
	110	0.078	0.961	0.951	0.0188	0.139
1.5	70	0.021	0.752	0.690	0.07	0.072
	90	0.012	0.983	0.973	0.0218	0.054
	110	0.159	0.927	0.908	0.0211	0.199

*Acid is the Acid concentrations of H_2SO_4 and Temp. is the temperatures of the hydrolysis; SS is the Sum of Squares; R^2 is the coefficient of regression and Adj. R^2 is the Adjusted coefficient of regression, and SE is the Standard Error

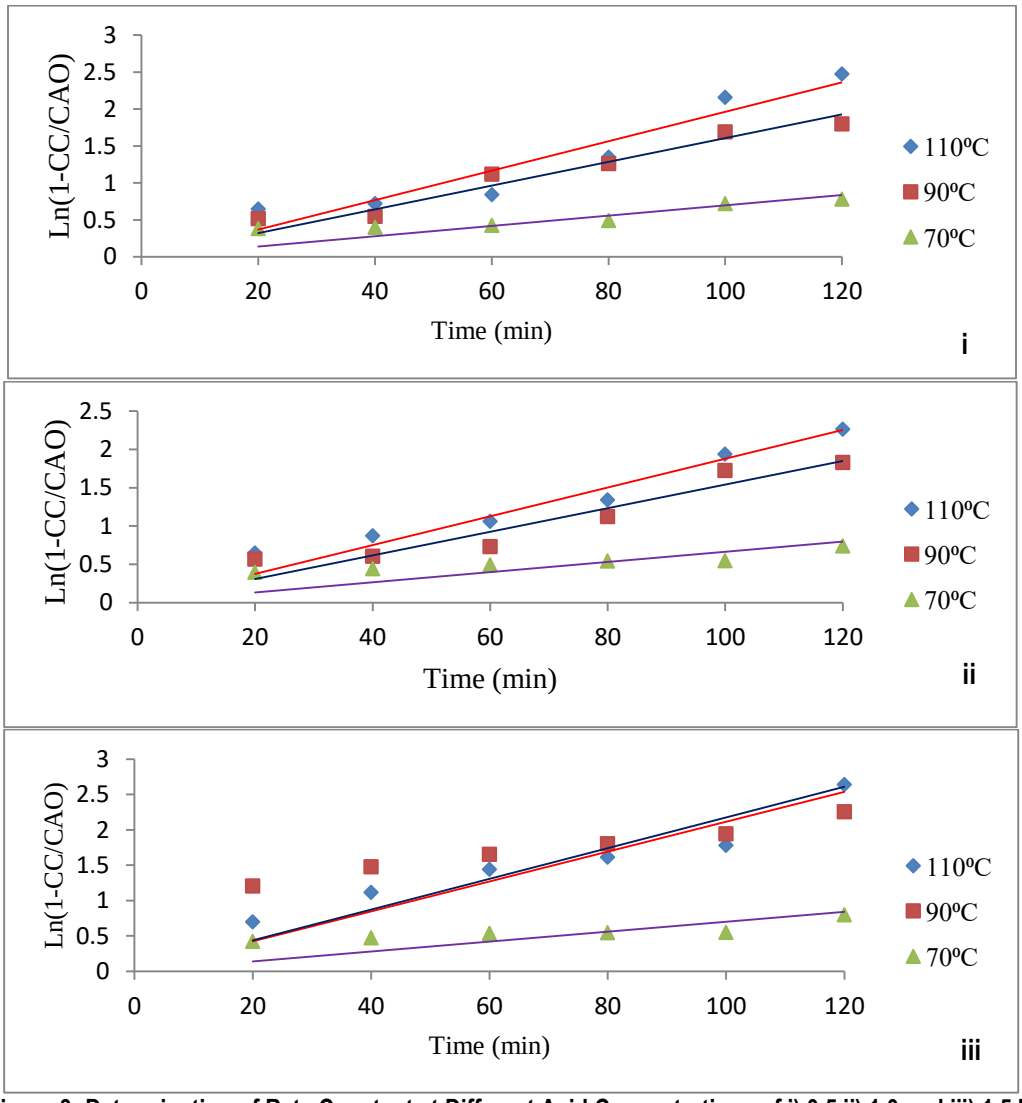


Figure 3: Determination of Rate Constant at Different Acid Concentrations of i) 0.5 ii) 1.0 and iii) 1.5 M

This agrees with the fact that the catalyst works by lowering the activation energy (Ea) for a reaction to proceed and drastically increasing the rate of the reaction (Roman & Winter, 2004; Sarma et al., 2014). It could also be deduced from the table that the values of enthalpy change (ΔH) for the hydrolysis are positive; indicative of an endothermic reaction. Incidentally, the values obtained for the ΔH show a massive increase with temperature, demonstrating the comparative susceptibility of this factor to the reaction temperature in the range of 70 - 110°C investigated for different acid concentrations. Based on this result, yam peel can readily be hydrolyzed as it is with other hemicellulose materials. The values obtained (Table 4b) at acid concentrations and temperatures for the entropy change (ΔS) are negative, and are indicative of the stability of the glucose syrup formed through the hydrolysis; as negative entropy indicates the increased degree of order in the system. This outcome is explained by the reaction not changing in phase or volume during the process (Tizazu & Moholkar, 2018).

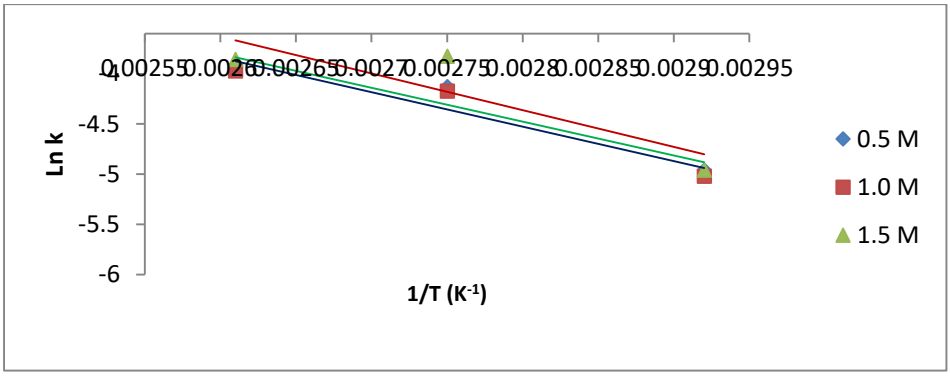


Figure 4: Plot of Arrhenius Equation to Evaluate Activation Energy and Frequency Factor

Table 4a: Determination of Activation Energy (Ea) and Frequency Factor

Acid (M)	SS	R^2	Adj. R^2	Slope (Ea/R)	SE (Slope)	Intercept (A)	SE (Intercept)
0.5	5.89E-03	0.996	0.9064	-3.38E+03	101.39	1.4542E+02	0.407
1.0	5.78E-04	0.996	0.9061	-3.43E+03	103.41	1.619E+02	0.415
1.5	6.18E-04	0.990	0.760	-3.67E+03	156.31	3.6952E+02	0.627

*A is the Arrhenius factor

Table 4b: Thermodynamic parameters of the hydrolysis

Acid (M)	A	E_a (Jmol^{-1})	ΔH x 10^3 (Jmol^{-1})			-ΔS x 10 (Jmol^{-1})			ΔG x 10^4 (Jmol^{-1})		
			ΔH_{343}	ΔH_{363}	ΔH_{383}	ΔS_{343}	ΔS_{363}	ΔS_{383}	ΔG_{343}	ΔG_{363}	ΔG_{383}
0.5	145.42	28100	25200	25100	24900	76.5	75.8	75.1	51500	52600	53700
1	161.9	28500	25700	25500	25400	75.6	74.9	74.2	51600	52700	53800
1.5	369.52	30500	27700	27500	27300	73.8	73.1	72.4	53000	54000	55100

There is a decrease in the values of ΔS as the temperature increases from 70 to 110°C. Similar patterns were also observed when the acid concentrations increased from 0.5 to 1.5 M. Conversely, the hydrolysis at 0.5 M acid concentration and 70°C temperature, on the other hand, exhibited a large negative entropy (ΔS) of 7.65 x 10 Jmol^{-1} than the other conditions. This is a sign that the glucose syrup produced in this condition is more stable than it is in other conditions of hydrolysis (Sarma et al., 2014).

Table 4b also included the ΔG results of hydrolyzing yam peel at various temperatures and H_2SO_4 concentrations. The reaction's non-spontaneity is demonstrated by the positive ΔG value that was achieved. The values of the ΔG for the hydrolysis show an increase from 5.15 x 10^4 Jmol^{-1} to 5.51 x 10^4 Jmol^{-1} as the temperature rises from 70 to 110°C. This

demonstrates that the hydrolysis of yam peel is a thermodynamically favored process (Tizazu & Moholkar, 2018). Similarly, the ΔG values increased from 5.15 x 10^4 $Jmol^{-1}$ to 5.51 x 10^4 $Jmol^{-1}$ with the increase in the H_2SO_4 concentration from 0.5 to 1.5 M. The patterns in the thermodynamic coefficients of ΔH, ΔS, and ΔG for the hydrolysis of yam peel showed that the thermodynamic parameters are affected by the different acid concentrations and temperatures investigated in this study. This is comparable to the study of Swati et al. (2013), which concluded that stable depolymerized products like glucose syrup are formed more readily at higher hydrolysis temperatures and higher acid concentrations (Tizazu & Moholkar, 2018). By reducing Gibb's Free Energy of activation (ΔG), the reaction rate is inversely proportional to the development of the transition state complex (Sarma et al., 2014). It can be seen from the thermodynamic parameter values that the ΔH and ΔS values play a crucial role in regulating reaction rates. The entropy of activation values that are negative shows that the activated complex is visible. According to the high negative quantity of activation entropy, the reaction could happen between neutral molecules or ions with like-charged ions and may generate a stiff intermediate transition state that causes the reaction to proceed slowly. Since the frequency factor values are below 1010, the current reaction may be occurring amongst ions with similar charges. Also, the values of the activation entropy that are negative could be due to the imine linkage's nitrogen atom holding up the protonated water molecule. The creation of the activated complex results in the solvent molecules being extensively reoriented, as shown by the significant negative values of ΔS (Ajala et al., 2018).

According to Starkweather Jr (1981), the activated complex is more ordered than the reactant when the value of ΔS is negative. A more negative ΔS value predicts a smaller value for frequency factor A and a slower reaction. At a given temperature, a higher value of ΔG will be seen for slower reactions because as the temperature rises, the rate of hydrolysis increases. The rate law temperature dependence was sufficiently well correlated using the Arrhenius function for the hydrolysis.

3.5 Biochemical Profiling of Yam Peel Hydrolysate

3.5.1 Phytochemical characterization

Table 5 presents the phytochemical evaluation of the yam peel hydrolysate which revealed the presence of chemical compounds such as alkaloid, phenol, tannin, flavonoid, glycoside, saponin, and steroid. The aforementioned metabolites possess numerous biological and therapeutic properties. For instance, the alkaloid has a collection of pharmacological activities which include analgesia, muscle relaxation, local anesthesia, and cardiac stimulation (Willie et al., 2021). Other researchers have also marked these compounds to protect the human body from free radicals, possess strong antioxidant, and improves the normal metabolism of aerobic cells (Mayasankaravalli et al., 2020). Therefore, the phytochemicals present in the yam peel hydrolysate show it is a good raw material for pharmaceutical industries. Apart from the fact that the hydrolysate is suitable for drug syrup making, the presence of these organic compounds adds to the medicinal value of the yam peel hydrolysate.

Table 5: Phytochemical properties of yam peel hydrolysate

Phytochemicals	Phytochemical detection
Alkaloid	+++
Phenols	++
Tannin	++
Flavonoid	+++
Glycoside	++
Saponin	++
Steroid	+

3.5.2 GC-MS determination of the bioactive chemical in the hydrolysate

The GC-MS profile of the yam peel hydrolysate reveals the presence of a total of 7 compounds as presented in Table 6. The table also contained the retention time (RT), peak area, and bioactivity of each of the compounds present in the hydrolysate. The bioactivities with the respective compound obtained indicate that the hydrolysate has the potential for pharmacological activity against bacterial and fungi pathogens (Suneetha et al., 2017). For instance, the cyclohexasiloxane dodecamethyl compound in the hydrolysate has bioactivities for skin-conditioning, antimicrobial, hair-conditioning, and antiseptic (Olivia et al., 2021). This further justifies that the yam peel hydrolysate is a good candidate for medicinal purposes. Also, various researchers as shown in Table 8 reported the bioactivities of the aforementioned compound in which they indicated that the compounds have antibacterial, antifungal, antioxidant, and anticancer properties (Suneetha et al., 2017).

Table 6: GC-MS analysis

S/N	RT	Compound name	Peak area (%)	Bioactivity
1	20.91	Cyclohexasiloxane, dodecamethyl	30.84	Useful as a de-foaming agent, anti-microbial, lubricant as well as an emollient in cosmetic products (Sheeba & Viswanathan, 2014).

2	25.24	Hexasiloxane, 1, 1, 3, 3, 5, 5, 7, 7, 9, 9, 11, 11-dodecamethyl	30.80	It is also an agent of emollient, anti-microbial, anti-septic, hair, and skin conditioning (Kumar, 2018).
3	29.12	Silane, [4- (1, 2 -bis [(trimethylsilyl) oxy] ethyl] - 1, 2 -phenylene] bis (oxy)] bis [trimethyl –	17.14	Antimicrobial and antioxidant (Hamdi, Puerta, & Valerga, 2008) (Kyomuhimbo et al., 2019)
4	31.53	Carbamate, N - (2 -naphthyl)-, 3 pentynyl ester	3.05	It is an antioxidant agent (Jacintha et al., 2016)
5	32.49	Cyclononasiloxane, octadecamethyl	7.70	Antimicrobial, cancer preventive, and chemo-preventive. It possesses antioxidant activity, useful in the food and pharmaceutical industries, as well as in traditional medicine (Sagaya & Rani, 2016).
6	35.51	Octasiloxane, 1, 1, 3, 3, 5, 5, 7, 7, 9, 9, 11, 11, 13, 13, 15, 15 - hexadecamethyl-	4.80	Antimicrobial, Antioxidant (Kumar et al., 2018; Mohammed et al., 2020).
7	38.26	Benzoic acid 2 6-bis (trimethylsilyl)oxy - trimethylsilyl ester	3.12	Antifungal, anti-bacterial (Muhammad et al., 2016).

3.5.3 FTIR evaluation of the hydrolysate

The functional groups present in the hydrolysate of the yam peel were identified using the FTIR spectrum and shown in Figure 5. The results of the FTIR peak values are represented in Table 7. Similar to that reported for the FTIR spectra analysis for cassava by Ajala (2018), the spectra are grouped, based on the range of 4000–400 cm^{-1}, into four regions: the X–H stretching region (4000–2500 cm^{-1}), the triple-bond region (2500–2000 cm^{-1}), the double-bond region (2000–1500 cm^{-1}) and the fingerprint region (1500–600 cm^{-1}) (Sacithraa et al., 2013).

The peaks obtained in the region of 4000–2500 cm^{-1} are 3445.91 cm^{-1} which are due to O–H stretch free that represents the intermolecular and intramolecular H bonds of free OH in cellulose materials (Sharif et al., 2015); and 2936.15 cm^{-1}, an indication of C-H stretch. The presence of O-H in the hydrolysate indicates alcohol which makes the hydrolysate of yam peel a more efficient glucose syrup for biofuel production (Madukosiri, 2013). The presence of C-H shows that the hydrolysate is rich in lipids as the lipids are abundant in the CH_2 functional group (Ogbaga et al., 2017). The bands obtained in the range of 2500 – 2000 cm^{-1} regions are 2473.88 and 2059.10 cm^{-1} which correspond to strongly -OH-bonded. The peak at 2318.73 cm^{-1} shows carboxylic acids which have a carbonyl group and an alcohol group. The groups share some fundamental physicochemical properties with aldehydes, ketones, and alcohols as reported by Khan et al. (2018). Meanwhile, all carboxylic acid ester exhibits excellent antifungal activity. The aldehyde which includes glutaraldehyde, formaldehyde, and cinnamaldehyde can be used in making household chemicals. Glutaraldehyde can be used as a sterilant and disinfectant as it has a broad spectrum of activity against bacteria, fungi, and viruses. Formaldehyde and Cinnamaldehyde are also used as a fungicide (Khan et al., 2018). The double-bond region of 2000 and 1500 cm^{-1} showed C=O stretching at 1641.16 cm^{-1} (Farias et al., 2014). The peak was the characteristic peak of the carbonyl (C=O) stretching vibration from the free carboxylic acid, esters, and fatty acids (Khan et al., 2018; Ofora et al., 2014; Sharif et al., 2015). The spectra in the fingerprint region indicate the presence of C-H vibration of aromatic ring at 1353.03 cm^{-1}, O-H phenolic at 1207.39 cm^{-1}, C-O stretch at 1137.73 cm^{-1} may be assigned to C-O stretching vibration from alcoholic groups, O-C=O at 1121.90,1093.40 and 1049.08 cm^{-1}, 627.97 cm^{-1} for C-Cl/β-glucosidic bonds between sugars (Guilherme et al., 2015; Shah et al., 2015). The presence of a band in the region of 1197.89 cm^{-1} is evidence of the existence of acid groups (such as carboxylic) (Jorgettoa et al., 2014). The presence of C-O-C functional groups in the hydrolysate indicates that the yam peel hydrolysate is very rich in glucose concentration since carbohydrates are dominated by vibrations of C-O-C or C-O functional groups (Ogbaga et al., 2017). However, the C-O-C stretching at 1023.75 cm^{-1} could mean the presence of unconverted polysaccharides in the hydrolysate (Buensanteai et al., 2012). The peaks in the regions 2942.48, 1634.83 to 1337.20, and 1102.90 to 1023.75 cm^{-1} correspond to lipids, amides, and carbohydrates, respectively (Jiang et al., 2012; Liu et al., 2013; Meng et al., 2014; Ogbaga et al., 2017). Therefore, the yam peel hydrolysate could be said to have contained methionine, tryptophan, phenylalanine, glucoside units, thiamine, and other amino acids. The bands observed confirmed that the hydrolysate comprises carbon, hydrogen, and nitrogen (Jorgettoa et al., 2014).

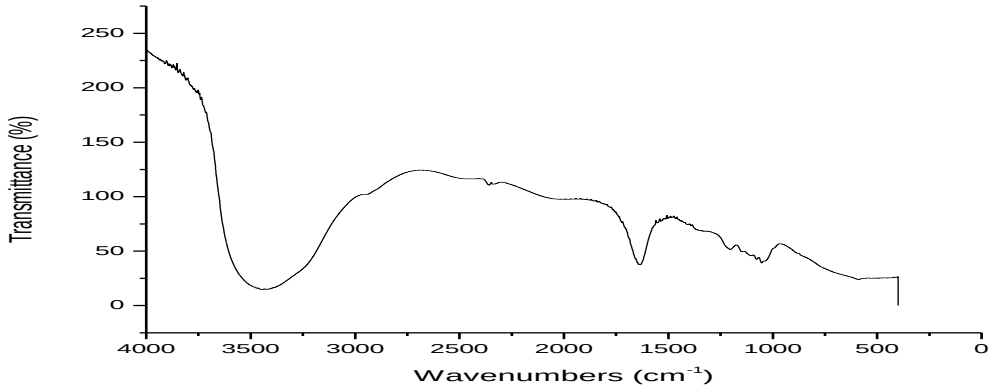


Figure 3: FTIR Spectra of Yam Peel Hydrolysate

Region	Wave number (cm^{-1})	Functional group	Inference
X–H stretching			
	3445.91	O-H stretch free	Alkanols, phenols, and AROH
	2936.15	C-H stretch	Alkyl groups CH_3, CH_2, CH
Triple-bond			
	2473.88	Strongly -OH- bonded	Alkanols, ROH
	2059.10		
Double-bond			
	1641.16	C=O stretch	Carbonyls, aldehydes, and alkanoates
Fingerprint			
	1353.03	The C-H vibration of the aromatic ring	
	1207.39	O-H phenolic	
	1137.73	C-O stretch	Ethers, R-O-R’
	1121.90,1093.40, 1049.08	O-C=O	
	627.97	C-Cl or β – glucosidic bonds between sugars	

Table 7: Functional groups in the hydrolysate

4.0 CONCLUSION

This study investigated the effects of acid concentrations and temperatures on the hydrolysis of yam peels in a kinetics process using a first-order reaction model. The model aided in establishing the optimal conditions for the hydrolysis as 1.5 M acid concentration and 110^{o}C temperature which yielded the highest GS of 46.44 g/l from a YP concentration of 50 g/l. The determined values of kinetic and thermodynamic parameters broadly revealed that the hydrolysis is affected by the process conditions of the acid concentration and temperature as they were confirmed to be important in improving the yield of glucose syrup. Additionally, the thermodynamic parameters showed that the glucose syrup (GS) is a “stable product.”

Besides being a low-cost, inexpensive substrate, and easily accessible, the use of yam peels in the food industry can be considered a significant way to reduce costs. This is due to the presence of numerous biochemical compounds in the yam peel hydrolysate which are a worthy substrate for pharmaceutical, beverages, and other purposes for human consumption. Also, it is noteworthy that the process of producing hydrolysate from yam peels would no doubt have a significant environmental impact. As it would help to resolve the problem associated with the disposal of yam waste. This would create a safe and eco-friendly environment, especially in the significant yam processing region of the world.

REFERENCES

Agler, M. T., Wrenn, B. A., Zinder, S. H., & Angenent, L. T. (2011). Waste to bioproduct conversion with undefined mixed cultures: the carboxylate platform. *Trends in biotechnology, 29*(2), 70-78.

Ahongshangbam, S. K., & Shantibala Devi, G. A. (2017). Proximate analysis and mineral (elemental) composition of certain spices of *Manipur*, India. *International Research Journal of Pharmacy, 8*(1), 1-5. doi: 10.7897/2230-8407.08016

Ajala, E. O., Ajala, M. A., Tijani, I. A., Adebisi, A. A., & Suru, I. (2020). Kinetics modeling of acid hydrolysis of cassava (Manihot escalate Cranz) peel and its hydrolysate chemical characterization. *Journal of King Saud University - Science*, *32*(4), 2284–2292. https://doi.org/10.1016/j.jksus.2020.03.003

Ajala, E. O., Eletta, O. A. A., Ajala, M. A., & Oyeniyi, S. K. (2018). Characterization and evaluation of Chicken eggshell for use as a bio-resource. *Arid Zone Journal of Engineering, Technology, and Environment, 14*(1), 26-40.

Aletan, U. I. & Kwazo, H. A. (2019) Analysis of the proximate composition, anti-nutrients, and mineral content of *Maerua crassifolia* leaves. *Nigerian Journal of Basic and Applied Science*, 27(1), 89-96. http://dx.doi.org/10.4314/njbas.v27i1.12 ISSN 0794-5698.

Belakhdar, G., Benjouad, A., & Abdennebi, E. H. (2015). Determination of some bioactive chemical constituents from *Thesium humile* Vahl. *Journal of Material and Environmental Science, 6*(10), 2778-2783.

Bethel-Wali, J. U., Ohaga, B., Ogbu, I., & Asadu, C. O. (2023). Hydrolysis and analysis of agricultural wastes using mineral acids for possible glucose synthesis. *Advances in Research*, *24*(5), 138–148. https://doi.org/10.9734/air/2023/v24i5965

Buensanteai, N., Thumanu, K., Sompong, M., Athinuwat, D., & Prathuangwong, S. (2012). The FTIR spectroscopy investigation of the cellular components of cassava after sensitization with plant growth-promoting rhizobacteria, Bacillus subtilis CaSUT007. *African Journal of Microbiology Research, 6*(3), 603-610. doi: 10.5897/AJMR11.935

Chen, T., Xiong, C., & Tao, Y. (2018). Enhanced hydrolysis of cellulose in ionic liquid using Mesoporous ZSM-5. *Molecules, 23*(529), 1-10. doi: 10.3390/molecules23030529

Doughari, J. H., & Saa-Aondo, M. (2021). Phytochemical analysis of crude methanol extracts and antimicrobial activity of n-hexane fractions of methanol seed and pod extracts of prosopis africana on some selected microorganisms. *Pharmacologyonline*, *2*, 121–137.

Egbosiuba, T. C., Agbajelola, D. O., Abdulkareem, A. S., Okafor, J. O., & Jimoh, A. (2014). Production and characterization of bioethanol from cassava peel: alternative energy source. *Elixir Chemical Engineering, 71*, 25097-25105.

Farias, F. O., Jasko, A. C., Colman, T. A. D., Pinheiro, L. A., Schnitzler, E., Barana, A. C., *et al.* (2014). Characterization of Cassava bagasse and composites prepared by blending with low-density polyethylene. *Brazilian Archives of Biology and Technology, 57*(6), 821-830. doi: http://dx.doi.org/10.1590/S1516-8913201402506

Gaewchingduang, S., & Pengthemkeerati, P. (2010). Enhancing efficiency for reducing sugar from cassava bagasse by pretreatment. *International Journal of Environmental, Chemical, Ecological, Geological, and Geophysical Engineering, 4*(10), 477-480.

Guilherme, A. A., Dantas, P. V. F., Santos, E. S., Fernandes, F. A. N., & Macedo, G. R. (2015). Evaluation of composition, characterization, and enzymatic hydrolysis of pretreated sugar cane bagasse. *Brazilian Journal of Chemical Engineering, 32*(01), 23 - 33. doi: dx.doi.org/10.1590/0104-6632.20150321s00003146

Hashimi, A. M. (2021). Utilization of water yam (*Dioscorea alata*) as a source of ethanol. *Journal of Chemical Society of Nigeria*, *46*(1), 79–82. https://doi.org/10.46602/jcsn.v46i1.577

Hodge, D. B., Karim, M. N., Schell, D. J., & McMillan, J. D. (2008). Soluble and insoluble solids contribute to high-solids enzymatic hydrolysis of lignocellulose. *Bioresource Technology, 99*(18), 8940-8948.

Jacintha, T. M. A., Sarvana, G. A., Uthayakumari, F., & Santhana, M. (2016). GC-MS analysis of bioactive compounds in the leaf extracts of Capparis diversifolia WIGHT & ARN. - An endemic taxon of Southern Western ghats. *World Journal of Pharmaceutical Research*, *5*(12), 1333–1340. https://doi.org/10.20959/wjpr201612-7528

Jacobsen, S. E., & Wyman, C. E. (2000). Cellulose and hemicellulose hydrolysis models for application to current and novel pretreatment processes. *Applied Biochemistry and Biotechnology, 84–86*, 81-96. doi: 0273-2289/00/84–86/0081/$14.00

Jiang, G., Nowakowski, D. J., & Bridgwater, A. V. (2010). A systematic study of the kinetics of lignin pyrolysis. *Thermochimica Acta, 498*(1-2), 61-66.

Jiang, Y., Yoshida, T., & Quigg, A. (2012). Photosynthetic performance, lipid production and biomass composition in response to nitrogen limitation in marine microalgae. *Plant Physiology and Biochemistry, 54*, 70-77.

Jimoh, S., Ado, S., & Ameh, J. (2009). Simultaneous Saccharification and Fermentation of Yam Peel to Ethanol by Co-culture of Aspergillus niger and

Saccharomyces cerevisiae. *Biol. and J. for the Tropics, 6*(1), 96-100.

Jin, Y., Zhang, L., Yi, Z., Fang, Y., & Zhao, H. (2022). Waste-to-energy: biobutanol production from the cellulosic residue of sweet potato by *Clostridia acetobutylicum*. *Environmental Engineering Research*, *27*(5), 0–2. https://doi.org/10.4491/eer.2021.372

Jorgettoa, A. O., Silva, R. I. V., Saeki, M. J., Barbosa, R. C., Martines, M. A. U., Jorgea, S. M. A*., et al.* (2014). Cassava root husks powder as green adsorbent for the removal of Cu(II) from natural river water. *Applied Surface Science, 288*, 356–362. doi: http://dx.doi.org/10.1016/j.apsusc.2013.10.032

Kargarzadeh, H., Ahmad, I., Abdullah, I., Dufresne, A., Zainudin, S. Y., & Sheltami, R. M. (2012). Effects of hydrolysis conditions on the morphology, crystallinity, and thermal stability of cellulose nanocrystals extracted from kenaf bast fibers. *Cellulose, 19*(3), 855-866.

Khan, S., Shinwari, M. I., Haq, A., Ali, K. W., Rana, T., Badshah, M*., et al.* (2018). Fourier-transform infrared spectroscopy analysis and antifungal activity of methanolic extracts of *Medicago parviflora, Solanum nigrum, Melilotus alba, and Melilotus indicu*s on soil-borne phytopathogenic fungi. *Pakistan Journal of Botany, 50*(4), 1591-1598.

Kouamé, J., Gnangui, S. N., Koné, F. M. T., & Kouamé, L. P. (2017). Use of kinetic and thermodynamic parameters for the prevention of enzymatic browning of edible *Yam Dioscorea cayenensis-rotundata cv. "Zrèzrou". International Journal of Current Microbiology and Applied Sciences, 6*(11), 4176-4187. doi: https://doi.org/10.20546/ijcmas.2017.611.489

Kralj, A. K. (2007). Checking the kinetics of acetic acid production by measuring the conductivity. *Journal of Industrial and Engineering Chemistry, 13*(4), 631-636.

Kumar, D. G., Karthik, M., & Rajakumar, R. (2018). GC-MS analysis of bioactive compounds from ethanolic leaves extract of Eichhornia crassipes (Mart) Solms. and their pharmacological activities. *~ 459 ~ The Pharma Innovation Journal*, *7*(8), 459–462. www.thepharmajournal.com

Kupiainen, L., Ahola, J., & Tanskanen, J. (2014). Kinetics of formic acid-catalyzed cellulose hydrolysis. *BioResources, 9*(2), 2645-2658.

Kyomuhimbo, H. D., Michira, I. N., Mwaura, F. B., Derese, S., Feleni, U., & Iwuoha, E. I. (2019). Silver–zinc oxide nanocomposite antiseptic from the extract of Bidens pilosa. *SN Applied Sciences, 1*(681), 1-17. doi:10.1007/s42452-019-0722-y

Lenihan, P., Orozco, A., O'neill, E., Ahmad, M., Rooney, D., & Walker, G. (2010). Dilute acid hydrolysis of lignocellulosic biomass. *Chemical Engineering Journal, 156*(2), 395-403.

Lin, Y., & Tanaka, S. (2006). Ethanol fermentation from biomass resources: current state and prospects. *Applied microbiology and biotechnology, 69*(6), 627-642.

Liu, J., Mukherjee, J., Hawkes, J. J., & Wilkinson, S. J. (2013). Optimization of lipid production for algal biodiesel in nitrogen-stressed cells of Dunaliella salina using FTIR analysis. *Journal of Chemical Technology & Biotechnology, 88*(10), 1807-1814.

Liu, X., Lu, M., Ai, N., Yu, F., & Ji, J. (2012). Kinetic model analysis of dilute sulfuric acid-catalyzed hemicellulose hydrolysis in sweet sorghum bagasse for xylose production. *Industrial Crops and Products, 38*, 81-86. doi: https://doi.org/10.1016/j.indcrop.2012.01.013

Madukosiri, C. H. (2013). Comparative study of some varieties of cassava grown and consumed in Bayelsa State as prospective biofuel and energy food sources. *International Journal of Agricultural Policy and Research, 1*(6), 156-165.

Mayasankaravalli, C., Deepika, K., Esther Lydia, D., Agada, R., Thagriki, D., Govindasamy, C., Chinnadurai, V., Othman Gatar, O. M., Khusro, A., Kim, Y. O., & Kim, H. J. (2020). Profiling the phytoconstituents of Punica granatum fruit peel extract and accessing its in-vitro antioxidant, anti-diabetic, anti-obesity, and angiotensin-converting enzyme inhibitory properties. *Saudi Journal of Biological Sciences*, *27*(12), 3228–3234. https://doi.org/10.1016/j.sjbs.2020.09.046

Meng, Y., Yao, C., Xue, S., & Yang, H. (2014). Application of Fourier transform infrared (FT-IR) spectroscopy in the determination of microalgal compositions. *Bioresource Technology, 151*, 347-354.

Miller, G. L. (1959). Use of dinitro salicylic acid reagent for determination of reducing sugar. *Biotechnology and Bioengineering Symposium, 5*, 193-219.

Mohammed, K. A. A., Wasfy, A. A. H. F., & Bazalou, M. S. (2020). Comparison of bioactive components of clove buds as extracted by two different methods and analyzed by gas chromatography triple quad time-flight technology. *International Journal of Pharmaceutical Quality Assurance*, *11*(4), 439–451. https://doi.org/10.25258/ijpqa.11.4.1

Moshi, A. P., Hosea, K. M. M., Elisante, E., Mshandete, A. M., & Nges, I. A. (2015). Production of bioethanol from wild Cassava *Manihot Glaziovii* through various combinations of hydrolysis and fermentation in stirred tank bioreactors. *British Biotechnology Journal, 5*(3), 123-139.

Muhaimin, & Sri, S. (2017). *Kinetic study of hydrolysis of coconut fiber into glucose.* Paper presented at the

International Conference on Chemistry, Chemical Process and Engineering (IC3PE).

Muhammad, K., Md. Moklesur Rahman Sarker, & Mohd, S. M. (2016). Phytochemical investigation of ethanolic extract of *Pericampylus glaucus* leaves from Malaysia by GC-MS analytical technique. *International Journal of PharmTech Research, 9*(12), 410-416.

Mukherjee, A., Mandal, T., Ganguly, A., Ghosh, P. S., & Chatterjee, P. K. (2017). Investigations on the kinetics of acid-catalyzed hemicellulose hydrolysis derived from waste rice straw for the production of bio-ethanol. *Indian Journal of Science and Technology, 10*(11), 1-8. doi: 10.17485/ijst/2017/v10i11/92605

Ofora, P. U., Arinze, R. U., Nwokoye, J. N., Onyema, C. T., Ekwueme, I. J., & Okpalaunegbu, C. (2014). Modification of Cassava Residue into Carboxymethylcellulose. *World Engineering and Applied Sciences Journal, 5*(2), 36-39. doi: 10.5829/idosi.weasj.2014.5.2.1118

Ogbaga, C. C., Miller, M. A. E., Athar, H., & Johnson, G. N. (2017). Fourier transform infrared spectroscopic analysis of Maize (Zea mays) subjected to progressive drought reveals the involvement of lipids, amides, and carbohydrates. *African Journal of Biotechnology, 16*(18), 1061-1066. doi: 10.5897/AJB2017.15918

Okunlola, A., & Lawal, A. K. (2022). Modified bitter yam (*Dioscorea dumetorum*) starches as immediate and sustained release polymers in bilayer tablets of Metformin hydrochloride. *Journal of Pharmaceutics and Nanotechnology, 10*(4), 19–25. https://doi.org/10.4172/23477857.10.4.003.

Olaniyan, O. P., & Ajayi, E. O. (2021). Phytochemicals and in vitro, anti-apoptotic properties of ethanol and hot water extracts of Cassava (Manihot esculenta Crantz) peel biogas slurry following anaerobic degradation. *Clinical Phytoscience*, *7*(77), 1–11. https://doi.org/10.1186/s40816-021-00318-9

Olivia, N. U., Goodness, U. C., & Obinna, O. M. (2021). Phytochemical profiling and GC-MS analysis of aqueous methanol fraction of Hibiscus asper leaves. *Future Journal of Pharmaceutical Sciences*, *7*(1). https://doi.org/10.1186/s43094-021-00208-4

Omoruyi, U., Odogwu, C. A., Asworth, V. O., Sama, F. J., Aiwonegbe, A. E., Ogbeide, O. K., Unuigbe, C. A., & Irabor, E. E. I. (2022). Comparative study on bioethanol production from agro-waste feedstock via acid hydrolysis method using two different mineral acids as catalysts. *ChemSearch Journal*, *13*(2), 117–123. https://www.ajol.info/index.php/csj/article/view/243075

Onyelucheya, O. E., Adeyemo, O. E., & Onyelucheya, C. M. (2017). Mathematical modeling for the prediction of liquid glucose and xylose produced from Cassava peel. *American Journal of Engineering Research (AJER), 6*(5), 274-280.

Onyelucheya, O. E., Nwabanne, J. T., Onyelucheya, C. M., & Adeyemo, O. E. (2016). Acid hydrolysis of cassava peel. *International Journal of Scientific and Technology Research, 5*(01), 184-187.

Purwadi, R., Lestari, D., Lohoo, C. A., & Tirtaadji, J. L. (2021). The effect of size and solid content in hydrolysis of sweet potato starch using endogenous beta-amylase enzyme. *IOP Conference Series: Materials Science and Engineering*, *1143*(1), 012043. https://doi.org/10.1088/1757-899x/1143/1/012043

Rinaldi, R., & Schüth, F. (2009). Acid hydrolysis of cellulose as the entry point into biorefinery schemes. *ChemSusChem: Chemistry & Sustainability Energy & Materials, 2*(12), 1096-1107.

Roman, M., & Winter, W. T. (2004). Effect of sulfate groups from sulfuric acid hydrolysis on the thermal degradation behavior of bacterial cellulose. *Biomacromolecules, 5*(5), 1671-1677.

Sacithraa, R., MadhanMohan, M., & Vijayachitra, S. (2013). *Quantitative Analysis of Tapioca Starch using FT-IR Spectroscopy and Partial Least Squares.* Paper presented at the International Conference on Innovations In Intelligent Instrumentation, Optimization, And Signal Processing "ICIIIOSP-2013".

Sagaya, G. R., & Rani, J. (2016). Screening of bio-active compounds and anticancer activity of *Punica granatum l. World Journal of Science and Research, 1*(3), 06-15.

Sarma, R., Dolui, A. K., & Kumar, A. (2014). Thermodynamic and kinetic studies of α-amylase catalyzed reaction in free and Carrageenan/Chitosan immobilized state. *Asian Journal of Chemistry, 26*(3), 725-728.

Sebayang, A. H., Hassan, M. H., Ong, H. C., Dharma, S., Silitonga, A. S., Kusumo, F.*, et al.* (2017). Optimization of reducing sugar production from *Manihot glaziovii* starch using Response Surface Methodology. *Energies, 10*(35), 1-13. doi: 10.3390/en10010035

Shah, P. U., Raval, N. P., & Shah, N. K. (2015). Adsorption of copper from an aqueous solution by chemically modified Cassava starch *Journal of Materials and Environmental Science, 6*(9), 2573-2582.

Sharif, N. F. A., Abd Razak, S. I., Abdul Rahman, W. A. W., Nayan, N. H. M., Rahmat, A., & Yahyad, M. Y. (2015). Cassava leaf composites. *BioResources, 10*(3), 4339-4349.

Sheeba, G. D., & Viswanathan, P. (2014). GC-MS Analysis of Phytocomponents in *Spermacoce articularis L. f.* leaf. *Research in Pharmacy, 4*(4), 01-07.

Starkweather Jr, H. W. (1981). Simple and complex relaxations. *Macromolecules, 14*(5), 1277-1281.

Stumm, W., & Morgan, J. J. (2012). *Aquatic chemistry: chemical equilibria and rates in natural waters* (Vol. 126): John Wiley & Sons.

Swati, G., Haldar, S., Ganguly, A., & Chatterjee, P. (2013). Investigations on the kinetics and thermodynamics of dilute acid hydrolysis of *Parthenium hysterophorus L.* substrate. *Chemical Engineering Journal, 229*, 111-117.

Tizazu, B. Z., & Moholkar, V. S. (2018). Kinetic and thermodynamic analysis of dilute acid hydrolysis of sugarcane bagasse. *Bioresource Technology, 250* 197–203. doi: https://doi.org/10.1016/j.biortech.2017.11.032

Villadiego-del Villar, A. E., Sarmiento-Zea, N., León-Pulido, J., & Rojas-Pérez, L. C. (2021). Bioethanol production from yam (*Dioscorea rotundata*) using simultaneous saccharification and fermentation (SSF). *TecnoLógicas*, *24*(50), e1724. https://doi.org/10.22430/22565337.1724

Wahyusi, K. N., Panjaitan, R., Sholikah, A. M., & Zakaria, V. (2022). Hydrolysis of starch from various tuber using acetic acid as an alternative sugar. *MATEC Web of Conferences*, *372*, 03008. https://doi.org/10.1051/matecconf/202237203008

Wanasundera, J., & Ravindran, G. (1994). Nutritional assessment of yam (Dioscorea alata) tubers. *Plant Foods for Human Nutrition, 46*(1), 33-39.

Wanasundera, J., & Ravindran, G. (2014). Nutritional assessment of yam (Dioscorea alata) tubers. *Plant Foods for Human Nutrition, 46*(1), 33-39.

Willie, P., Uyoh, E. A., & Aikpokpodion, P. O. (2021). Gas chromatography-mass spectrometry (GC-MS) assay of bio-active compounds and phytochemical analyses in three species of apocynaceae. *Pharmacognosy Journal*, *13*(2), 383–392. https://doi.org/10.5530/pj.2021.13.49

Woiciechowski, A. L., Nitsche, S., Pandey, A., & Soccol, C. R. (2002). Acid and enzymatic hydrolysis to recover reducing sugars from cassava bagasse: An economic study. *Brazilian Archives of Biology and Technology, 45*(3).

Xiang, Q., Lee, Y., Pettersson, P. O., & Torget, R. W. (2003). Heterogeneous aspects of acid hydrolysis of α-cellulose *Biotechnology for Fuels and Chemicals* (pp. 505-514): Springer.

Yusuf, A., Elinge, C. M., Hannatu, A., & Senchi, D. S. (2020). Comparative study of bioethanol potentials produced from yam peels and *Bambara* nut shells. *International Journal of Advanced Academic Research (Sciences, Technology and Engineering)*, *6*(10), 82–94. https://doi.org/10.46654/ij.24889849

Zhang, M., Jia, H., Wang, B., Ma, C., He, F., Fan, Q., & Liu, W. (2023). A prospective review on the research progress of citric acid-modified starch. *Foods*, *12*(458), 145–203. https://doi.org/10.1201/9781420080247-c8

Zhao, Y., Wang, Y., Zhu, J., Ragauskas, A., & Deng, Y. (2008). Enhanced enzymatic hydrolysis of spruce by alkaline pretreatment at low temperature. *Biotechnology and Bioengineering, 99*(6), 1320-1328.