

Acid Hydrolysis Of Cassava Peel

Onyelucheya Okechukwu Elechi, Nwabanne Joseph Tagbo, Onyelucheya Chioma Mary, Adeyemo Oluseun Emmanuel

Abstract: The aim of this work is to study the hydrolysis process of cassava peel using phosphoric acid. The substrate was characterised using proximate analysis and result obtained showed that cassava peel has high hemicellulose content. The effect of process variables; acid concentration (2.5wt%, 5wt%, 7.5wt% and 10wt %) and time variation on glucose and xylose yield were studied. The maximum glucose was obtained as 2.218mg/ml at the following conditions: 7.5wt%, 1mins and 121°C while the maximum xylose was obtained as 33mg/ml under the following conditions; 10wt%, 3mins and 121°C. The Saeman's model and two-fraction were used to fit the experimental data for glucose and xylose yield and two-fraction model gave the best fit for both. In conclusion cassava peel as shown by the results obtained can be used for the production of glucose and xylose.

Index Terms: acid hydrolysis, cassava peels, cellulose, glucose concentration, xylose concentration, saeman model, two- fraction model.

1 INTRODUCTION

Lignocellulose is the major structural component of woody plants and non-woody plants. They are a natural, abundant and renewable resource. Examples of sources of lignocellulosic materials are agricultural wastes (corn stover, sugarcane bagasse, flax straw, potato pulp, cassava bagasse, cowpea husk, rice husk, soya beans husks), forestry (beech bark, beech wood, populus tremuloides wood) and herbaceous materials (e.g. reed grass, switch grass, ryegrass). Cassava peel is one of the numerous Lignocellulosic agriculture waste generated in Nigeria. According to [1], a large amount of wastes is typically produced annually from cassava processing, amounting to about 30 million tonnes. Another study by [2], says that a cassava starch production unit processing 100 tons of tubers per day has an output 47 tons of fresh by-products, which may cause environmental problems when left in the surroundings of processing plants or carelessly disposed of. Improper disposal of waste causes environmental problems. According to [3], the use of cassava by-products as feedstuffs or as an alternative substrate for biotechnological processes is a positive way to alleviate environmental issues, hence the need for this work. This agriculture waste biomass consists of cellulose, hemicellulose, lignin and other materials called extractives [4]. Hemicellulose when hydrolysed gives xylose, arabinose, galactose and mannose. Cellulose when hydrolysed gives glucose. The chemical properties of the components of lignocellulosics make them a substrate of enormous biotechnological value [5]. Conversion of these wastes to valuable products such as glucose, xylose, arabinose, furfural etc. provides a more efficient means of waste management.

One of the steps involved in the conversion of lignocellulosic materials is hydrolysis. This can be done using enzymes or acids. Understanding the kinetic models involved in the hydrolysis process is an important step in successful conversion of these wastes to useful products. The aim of this work is to study the hydrolysis process of cassava peel using phosphoric acid. The following are the objectives of the study: to study the effect of process variables (time and acid concentration) on glucose and xylose yield and to study the kinetic models (Saeman and Two-fraction) as it fits the data obtained.

2 MATERIALS AND METHODS

2.1 Characterization

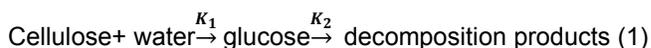
The cassava peels were thoroughly washed with clean water to remove the unwanted material after which it was sun dried. The size of the dried cassava peel was reduced with the aid of grinding machine and screened to 0.1 mm diameter. The cellulose and hemicellulose composition were measured according to [6]. The lignin content of the substrates was measured using the standard procedure of the Association of Official Analytical Chemists [7].

2.2 Acid Hydrolysis

5g of the sample was added to 50ml of 2.5wt% of phosphoric acid. The samples were hydrolysed for 5 minutes at 121°C in an autoclave. After 5 minutes the reaction was quenched using an ice bath. The glucose and xylose concentration of the filtrate were measured using DNS (3, 5- Di nitro Salicylic Acid) method [8] at the absorbance of 540nm and 480nm respectively. The same procedure was repeated for 10, 15, 20, 30, 40, 50, 60, 70, 80, and 90 minutes. Acid concentrations were also varied at 5.0wt%, 7.5wt% and 10wt%.

2.3 Kinetic Study

Saeman model [9] was used to fit the experimental data and reaction proceeds as shown in equation (1).



Where k_1 is the rate of conversion of cellulose to glucose and k_2 is the rate of decomposition of glucose. Both have units of the reciprocal of time (min^{-1}). Both reactions were considered to be first order and irreversible. Assuming homogeneous first-order reactions with excess water, and solving equation (1) gives equation (2).

- Onyelucheya, Okechukwu Elechi Chemical Engineering, Federal University of Technology Owerri, Owerri, Nigeria, +2348033691707 (e-mail: okechukwu.onyelucheya@futo.edu.ng)
- Nwabanne, Joseph Tagbo, Chemical Engineering, Nnamdi Azikiwe University, Awka, Nigeria, +2348066115176., (e-mail: jt.nwabanne@unizik.edu.ng)
- Onyelucheya, Chioma Mary*, Chemical Engineering, Federal University of Technology Owerri, Owerri, Nigeria, +2348030927060, (e-mail: conyelucheya@yahoo.com).
- Adeyemo Oluseun Emmanuel, Chemical Engineering, Federal University of Technology Owerri, Imo state Nigeria, (email: oluseunadeyemosewe@gmail.com)

$$G = \left(\frac{k_1 C_0}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \quad (2)$$

It is assumed that all the cellulose and hemicellulose hydrolyses to glucose and xylose respectively; therefore the initial cellulose concentration, C_0 (in gL^{-1}) is equal to the potential concentration of glucose and xylose, G_{n0} obtainable from the cellulose and hemicellulose respectively. Equation (2) becomes:

$$G = \left(\frac{k_1 G_{n0}}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \quad (3)$$

Lavarack et al [10] modified the Seaman model by the introduction of α into the Seaman's model. α is the ratio of fast hydrolysable glucan to total glucan, the value is less than or equal to 1. Two-fraction model is given by equation (4).

$$G = \alpha \left(\frac{k_1 G_{n0}}{k_2 - k_1} \right) (e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

G_{n0} can be determined analytically as described by [11] in equation (5)

$$G_{n0} = \frac{FZ\rho}{LSR} \quad (5)$$

Where F is stoichiometric factor due to hydration of molecule during the hydrolysis, ρ is the density of hydrolysis, z is composition of the raw material for the polysaccharides and LSR is the liquid to solid ratio. In this work the Seaman and Two-fraction models were used to model the glucose and xylose yield from the hydrolysis of cassava peels using phosphoric acid. The rate constants were obtained from the models using MatLab 7.5.0 software.

3. RESULT AND DISCUSSION

3.1. Cassava peel composition

The result obtained from the analysis of the cassava peel showed a hemicellulose composition of 29.81%, cellulose-3.05% and lignin- 2.65%. Aderemi and Nworgu [12], obtained cellulose- 5.40%, hemicellulose- 21.65% and lignin- 4.81%.

3.2. Effect of acid concentration and time variation on glucose and xylose yield

Fig. 1 shows the glucose yield obtained from cassava peel hydrolysed with 2.5%, 5%, 7.5% and 10% phosphoric acid. Using 2.5% acid concentration, the glucose yield was observed to increase gradually and reached its peak (1.52 mg/ml) after 30 mins of reaction time. However there was a decline in glucose yield as time increased. Maximum glucose of 1.703mg/ml was obtained at 20mins when 5% acid concentration was used. This concentration of acid was observed to have attained its maximum glucose earlier when compared to 2.5% acid concentration and also experienced a decline in yield as time increased. At 7.5% acid concentration, the maximum glucose was obtained at 5mins and afterwards the glucose yield decreased rapidly. A similar trend was observed at 10% acid concentration. From these results it can be observed that as acid concentration increased, peak yield was obtained at shorter time. Therefore increasing the acid concentration will reduce the time required for acid hydrolysis. It was also observed that a highest glucose yield (2.499mg/ml) was obtained at 7.5% acid concentration which indicates that

increase in acid concentration to this point caused more release of glucose. However increase to 10% acid concentration decreased the yield obtained, but it is possible that high glucose concentration can be obtained at reaction time between 0-5 mins. Akponah and Akpomie [13] obtained a glucose concentration of 250mg/g from acid hydrolysate of cassava root peels under the following conditions: 0.6M H_2SO_4 , 90°C and 30 mins. The decrease in glucose yield indicates decomposition of glucose to degradation products as time increases. This however does not agree with the result obtained by [11], in which there was a continuous increase in glucose yield which indicates that no decomposition reaction occurred. Fig. 2 shows the xylose yield obtained from cassava peel hydrolysed with 2.5%, 5%, 7.5% and 10% phosphoric acid. From fig 2, the 2.5wt% acid concentration was observed to have a steady rise in its xylose yield until it attained its maximum xylose concentration (20.1995mg/ml) at 50mins. It however, experienced a gradual decrease due to the decomposition reaction. Using 5wt% acid, a similar trend of steady rise was also observed but the peak (25.121mg/ml) was attained after 40mins of reaction time. The maximum xylose yield of 31.8577mg/ml was obtained after 5min of reaction time for acid concentration of 7.5wt%, after which the yield started to decrease. This decline in yield as earlier stated is attributed to the decomposition of xylose to degradation products. Similar trend was observed with 10wt% acid concentration, where 33.0675mg/ml of xylose was obtained. Comparing xylose and glucose yield, xylose gave a higher yield and this is because of the high hemicellulose content of the cassava peel and the operating conditions as cellulose requires harsh conditions to be hydrolysed.

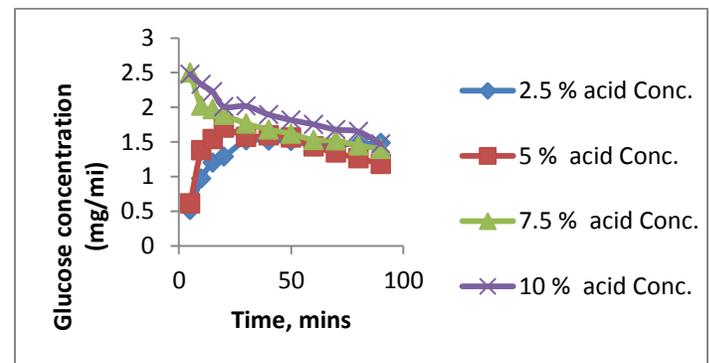


Fig. 1: Glucose yield obtained from cassava peel hydrolysed with 2.5%, 5%, 7.5% and 10% phosphoric acid.

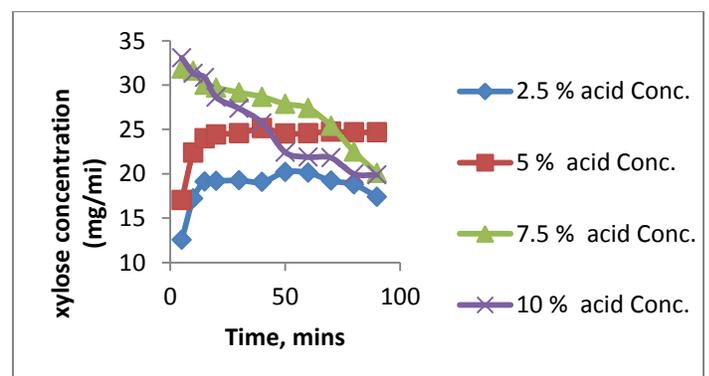
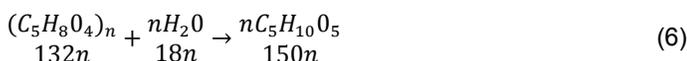
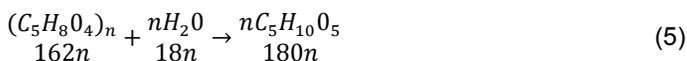


Fig. 2: Xylose yield obtained from cassava peel hydrolysed with 2.5%, 5%, 7.5% and 10% phosphoric acid.

3.3. Potential Glucose and Xylose Concentration

The potential concentration of glucose obtainable from cassava peel was calculated using equation (4). Where F is stoichiometric factor due to hydration of molecule during the hydrolysis was obtained for glucose as (180/162) from equation (5) and for xylose as (150/132) from equation (6). ρ is the density of hydrolysis-1890mg/ml, z is composition of the raw material for the polysaccharides- 3.05% g/g for glucose and 29.81%g/g. LSR is the liquid to solid ratio- 18.9g/g. Applying equation (4) potential glucose and xylose was calculated as 3.3889mg/ml and 33.8761mg/ml respectively.



3.4. KINETIC STUDY

The glucose concentration yield obtained from the experiment were fit into the Seaman and two-fraction models, tables 1 and 2 shows the kinetic parameters obtained from the two models respectively. The result obtained shows that two fraction model gave a better fit. This is based on the R^2 and adjusted R^2 value obtained for the two-fraction model. This result agrees with Aguilar et al [14] in their study. Based on the two-fraction model, the fractional value (α) obtained varied from 0.48 to 0.72, with an average value of 0.62. Rate of glucose production (k_1) was observed to increase with increase in acid concentration from 2.5% to 7.5%, after which there was a decrease in reaction rate at 10% acid concentration. This change that occurred at 10% phosphoric acid indicates that this concentration is not suitable for the substrate, as glucose yield will be low. From the kinetic data obtained, the optimum conditions selected are 7.5wt%, 121°C, 1min which will yield 2.2182mg/ml of glucose. Gámez et al [10] obtained 3.0g of glucose/L from hydrolysis of sugar cane bagasse using phosphoric acid under these conditions: 122°C, 4% acid concentration and 300mins. Aguilar et al [14] obtained 3g of glucose /L from hydrolysis of sugar cane bagasse under the following conditions: 2% H_2SO_4 , 122°C for 24 min. Table 3 and 4 shows the kinetic parameters obtained from fitting xylose yield into the Saeman's and two-fraction model. From the result obtained two fraction model gave a better fit. This agrees with what was obtained by Aguilar et al [14] and Rodriguez-Chong et al [15]. However this does not agree with [11], as the model obtained to fit kinetic modeling of xylose concentration was Saeman. This is based on comparing the R^2 and adjusted R^2 value obtained from both models. From the two-fraction model, k_1 was observed to be increasing as acid concentration increases. This means that xylose yield increased with acid concentration. The fractional value (α) obtained ranged from 0.60 to 0.98. The maximum xylose was obtained as 33mg/ml under the following conditions; 10wt%, 3mins and 121°C. Aguilar et al [14] obtained 21.6g of glucose /L from hydrolysis of sugar cane bagasse under the following conditions: 2% H_2SO_4 , 122°C for 24 min.

Table 1: Kinetic parameters obtained from Seaman's model for glucose yield

Conc. (wt %)	k_1 (min^{-1})	k_2 (min^{-1})	R^2	Adjusted R^2
2.5	0.0294	0.01552	0.9357	0.9292
5.0	0.04512	0.01864	0.9036	0.8939
7.5	0.1438	0.01605	0.3612	0.2973
10	0.1915	0.01304	0.6403	0.6043

Table 2: Kinetic parameter obtained from Two-fraction model for glucose yield

Conc. (wt%)	k_1 (min^{-1})	k_2 (min^{-1})	α	R^2	Adjusted R^2
2.5	0.08757	0.00153	0.4811	0.9946	0.9933
5.0	0.1029	0.006918	0.6018	0.9728	0.9667
7.5	5.980	0.005976	0.6595	0.9575	0.9480
10	3.516	0.005526	0.7173	0.9924	0.9908

Table 3: Kinetic parameters obtained from Seaman's model for xylose concentration yield

Conc. (wt %)	k_1 (min^{-1})	k_2 (min^{-1})	R^2	Adjusted R^2
2.5	0.0595	0.01106	0.8095	0.7904
5.0	0.1014	0.005681	0.8772	0.865
7.5	0.6179	0.004803	0.9867	0.9853
10	33.55	0.00698	0.9919	0.9902

Table 4: Kinetic parameters obtained from Two-fraction model for xylose concentration yield

Conc. (wt %)	k_1 (min^{-1})	k_2 (min^{-1})	α	R^2	Adjusted R^2
2.5	0.1902	0.001176	0.6019	0.9898	0.9875
5.0	0.2336	$4.29e^{-005}$	0.7306	0.9996	0.9995
7.5	0.7942	0.004395	0.9746	0.9828	0.9790
10	3.753	0.006485	0.9833	0.9919	0.9901

5. CONCLUSION

It can be concluded that cassava peel can be converted to glucose via hydrolysis using phosphoric acid. The maximum glucose was obtained at 7.5wt%, 121°C after 5 minutes reaction time. The experimental data obtained was also shown to be adequately described by two-fraction model.

REFERENCES

- [1] E. I. Ohimain, D. I. Silas-Olu, and J. T. Zipamoh, "Bio-wastes Generation by Small Scale Cassava Processing Centres in Wilberforce Island, Bayelsa State, Nigeria", Greener Journal of Environmental Management and Public Safety. vol. 2 (1), pp. 051-059, January 2013.
- [2] S. O. Aro, V. A. Aletor, O. O. Tewe and J. O. Agbede, "Nutritional potentials of cassava Tuber wastes: A case study of a cassava starch processing factory in south-western Nigeria", Livestock Research for Rural Development. vol 22, November 2010. Article 213. Retrieved June 23, 2015, from <http://www.lrrd.org/lrrd22/11/aro22213.htm>
- [3] Pandey, C. R. Soccol, P. Nigam, V. T. Soccol, L. P. S. Vandenberghe and R. Mohan, "Biotechnological potential of agro-industrial residues. II: cassava

- bagasse”, *Bioresource Technology*, vol 74 (1): 81-87 August 2000.
- [4] Ghose, T.K. “Cellulose biosynthesis and hydrolysis of cellulosic substances”, *Advances in Biochem. Eng.*, vol. 6, pp 39-76, 1956.
- [5] S. Malherbeand and T. E. Cloete, “Lignocellulose biodegradation: Fundamentals and Applications: A review”, *Environment, Science And Biotechnology*, vol. 1, pp 105-114, 2003.
- [6] E. W. Crampton and L. A. Maynard, “The Relation of Cellulose and Lignin Content to the Nutritive Value of Animal Feeds” , *Journal of. Nutrition*, vol 15, pp 383-395, (1938).
- [7] Association of Official Analytical Chemists, “Official Methods of Analysis”, Arlington Virginia USA 15th Edition. pp 69-88, 1990.
- [8] G. L. Miller, “Use of dinitrosalicylic acid reagent for the determination of reducing sugar”, *Analytical. Chemistry*, vol 31, pp 426 – 428.
- [9] J. F Saeman, “Kinetics of wood saccharification Hydrolysis of cellulose and decomposition of sugars in dilute acid at high temperature”, *Industrial and Engineering Chemistry*, vol 37, pp 43-52, 1945.
- [10] B.P. Lavarack, G. J. Griffin and D. Rodman, “The Acid Hydrolysis of Sugarcane Bagasse Hemicellulose to Produce Xylose, Arabinose and other Products”, *Biomass and Bioenergy*, vol. 23, pp 367-380, 2002.
- [11] S. Gàmez, J. J. González-Cabriales, J. Alberto Ramírez, G. Garrote and M. Vázquez, “Study of the hydrolysis of sugar cane bagasse using phosphoric acid”, *Journal of Food Engineering*, vol 74, pp 78–88, 2006.
- [12] F. A. Aderemi and F. C. Nworgu, “Nutritional Status of Cassava Peels and Root Sieviate Biodegraded With *Aspergillus niger*”, *American-Eurasian J. Agric. & Environ. Sci.*, vol 2 (3) pp 308-311, 2007.
- [13] E. Akponah and O.O. Akpomie, “Analysis of the suitability of yam, potato and cassava root peels for bioethanol production using *Saccharomyces cerevisiae*”, *International Research Journal of Microbiology*, vol. 2(10) pp. 393-398, 2011.
- [14] R. Aguilar, J.A Ramírez, G. Garrote and M. Vázquez, “Kinetic study of the acid hydrolysis of sugar cane bagasse”, *Journal of Food Engineering*, vol.55, 309–318 ,2002.
- [15] A. Rodriguez-Chong, J. A. Ramirez, G. Garrote and M.Vazquez, “Hydrolysis of sugar cane bagasse using nitric acid:A kinetic assessment”, *Journal of Food Engineering*, vol 61,143–152, 2004.