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Mathematical Modeling for the Prediction of Liquid Glucose and Xylose Produced From Cassava Peel

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ABSTRACT: *Hydrolysis of cassava peel was studied using nitric acid (with the concentration of 1.0 wt. %, 1. 5wt. %, 2.0 wt. % and 3.0 wt. %) at the reaction time of 0 to 27.5 minutes and temperature of 121ºC to determine the rate of generation and degradation of glucose and xylose. Seaman's and two-fraction models were used to determine the kinetic parameters. It was observed that the two-fraction model gave a better fit over Seaman's model Therefore with, k_1, k_2 and α known, a mathematical expression can be develop to determine the glucose and xylose yield at any time.*

Keywords: *Acid Hydrolysis, Seaman's model, Two-fraction model, Cassava peel, Kinetic parameters, Xylose and Glucose*

I. INTRODUCTION

Agricultural activities of man have led to the production of lignocellulosic materials such as wheat straw, rice straw, corn stover etc. which causes pollution if not properly disposed. For example, close to 731 million tons of rice straw is produced per annum globally (Africa: 20.9 million tons, Asia: 667.6 million tons, Europe: 3.9 million tons, America: 37.2 million tons, and Oceania: 1.7 million tons) [1]. Lignocellulosic materials are majorly made of cellulose, hemicellulose, lignin, carbohydrate, ash, lipid etc. These compositions vary from one lignocellulosic material to another for example potato peel composition was obtained as: 55.25% cellulose, 11.71% hemicellulose and 14.24% lignin [2] while rice straw composition was obtained as 27% hemicellulose, 39% cellulose and 12% lignin [3]. Cellulose is polysaccharides which compose of D-glucose units joined together by B-glycosidic linkage between C-1 of number unit and C-4 of the next glucose unit and the number of D-glucose unit in the cellulose varies from 300-2500 [4]. Cellulose on hydrolysis with dilute acid (e.g.) gives D-glucose. Hemicelluloses are the plant cell wall polysaccharides which have a close association with the cellulose. It is made up of pentose (xylose, arabinose), hexoses (glucose, mannose and galactose) and organic acids (glucuronic acid, galacturonics acids). In comparison to cellulose, it is easily hydrolysed [5]. Lignin occurs between cells and cell walls, it is formed during lignification of the plant tissue and has a close association with the cell walls, cellulose and hemicelluloses and give the plant a good strength and rigidity [6]. Due to the high rate of accumulation of lignocellulosic materials it is necessary to dispose them in such a way that would not have negative effect on the ecosystem.

For instance, large amount of wastes are generated during cassava processing: this contributes to environmental pollution [7]. According to statistics Nigeria produced 19, 043, 008 tons, Cameroon produced 1, 587, 872 and Togo produced 592, 867 tons in 1990. In 1997, Nigeria produced 32, 695, 000 tons, Cameroon produced 1, 918, 000 tons and Togo produced 595, 792. In 2003, Nigeria produced 33,379, 000 tons, Cameroon produced 2, 619, 142 tons and Togo produced 724, 000 tons [8]. This increase in production also means, increase in waste generated which are often left to decay in the open or burnt, emitting carbon dioxide to the atmosphere. But according to Pandey et al. [9] these problems can be prevented by the use of cassava by-products as feedstuffs or as an alternative substrate for biotechnological processes. One of the biotechnological processes that convert waste to useful product is fermentation. Fermentation of lignocellulosic materials is however preceded by hydrolysis. Hydrolysis reaction can either be by acids ($HCl, H_3PO_4, HNO_3, H_2SO_4$ etc.) or enzymes (e.g. $cellulase$). According to Wyman [10], dilute or concentrated acids breakdown the cellulose and hemicellulose polymers in lignocellulosic biomass to form individual sugar molecules which can be fermented into ethanol. The product of hydrolysis consists mainly of the following individual sugar molecules: glucose, xylose, arabinose, mannose and galactose. This research work is therefore focused on the mathematical model for the conversion of cassava peel to liquid glucose and xylose at different concentration of Nitric acid and also at different reaction time. This knowledge will aid in making decisions on expected glucose and xylose yield from cassava peel.

II. MATERIALS AND METHOD

Cassava peels used in this study were obtained from Eziobodo, Owerri West Local Government Area of Imo State, Nigeria. After the peels has been removed from the tuber they were thoroughly washed so as remove sand and other unwanted materials ,sundried in order to reduce the moisture content, milled so as to increase the surface area, screened to a fraction less than 0.5 mm diameter and stored for subsequent use.

Proximate analysis was carried out to determine the composition of the cellulose, hemicellulose and lignin. The cellulose and hemicellulose were determined according to ref. [11] while the lignin content was determined according to ref. [12]. Hydrolysis was carried out in an autoclave at 121ºC. 5g of the stored sample was weighed and put inside a beaker; 50ml of 1.0wt. % nitric acid was added to it and corked. The sample was hydrolysed for 5 minutes after which it was cooled in an ice bath so as to quench the reaction and finally filtered. The glucose and xylose in the filtrate was analysed by UV-VIS spectroscopy at 540nm and 490nm respectively using DNS (3, 5- Dinitro Salicylic Acid) method [13]. This procedure was repeated for 7.5, 10, 12.5, 15, 17.5, 20, 22.5, 25 and 27.5 minutes. Acid concentrations were varied at 1.5wt.%, 2.0wt. % and 3.0wt.%. All experiments were carried out in duplicates. The rate of generation and degradation at different concentration of acid for each sugar was determined by MATLAB 7.5.0.

III. RESULTS AND DISCUSSION

3.1 The proximate analysis of cassava peel

The composition of cassava used in this work is shown in Fig. 1 while reference [14] obtained cellulose-5.40%, hemicellulose-21.65% and lignin-4.81% for the same cassava peel. It can be deduced that cassava is richer in hemicellulose than cellulose unlike rice straw (cellulose-34.3%, hemicellulose-24.8% and lignin-15.8%) and wheat straw (cellulose-37.5%, hemicellulose-30.0% and lignin-16.5%) which are richer in cellulosic fraction than hemicellulosic fraction.

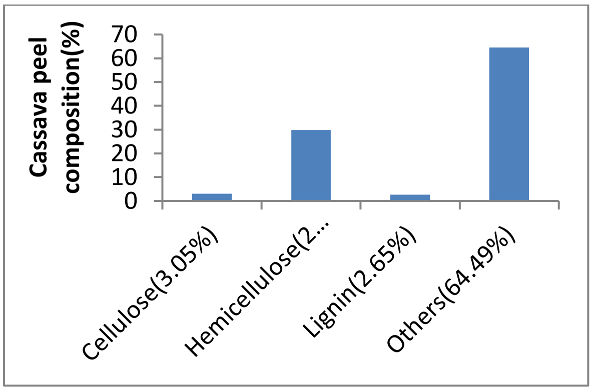


Fig.1: Composition of cassava peel

3.2. The study of glucose production

3.2.1 Effect of acid concentration and time variation on glucose yield

Fig. 2 shows the glucose yield with time at different concentration of nitric acids (1.0 $wt.\%$, 1.5 $wt.\%$, 2.0 $wt.\%$ and 3.0 $wt.\%$). With 1.0 $wt.\%$ nitric acid concentration, the glucose yield increased rapidly during the first 5 minutes of the hydrolysis and increased slightly for the next 2.5 minutes where it had maximum concentration of 0.4247 mg/ml after which the glucose began to decrease slightly. For 1.5 wt. % nitric acid concentration, the glucose yield increased at higher rate for the first 5 minutes of the experiment where 0.6392 mg/ml of glucose was obtained and then concentration of glucose began to reduce slightly. Using 2.0 wt. % nitric acid concentrations, glucose yield increased for the 5 minutes of the experiment and increased slightly for the next 2.5 minutes where 0.6599 mg/ml of glucose was achieved. With 3.0 wt. % nitric acid concentration, glucose had its maximum yield of 0.7582 mg/ml at 5 minutes after this point glucose concentration began to decline slightly.

From the result it can be observed that glucose production increase with an increase in acid concentration that highest production of glucose was achieved with 3.0 wt. % followed by 2.0 wt. % and 1.5 wt. %. It can be deduced that the concentration of the acid and time are determining factor in the production of glucose from cassava peel. Decrease in the concentration of sugar is associated to sugar decomposition and production of an inhibitor which is also in agreement with reference [1].

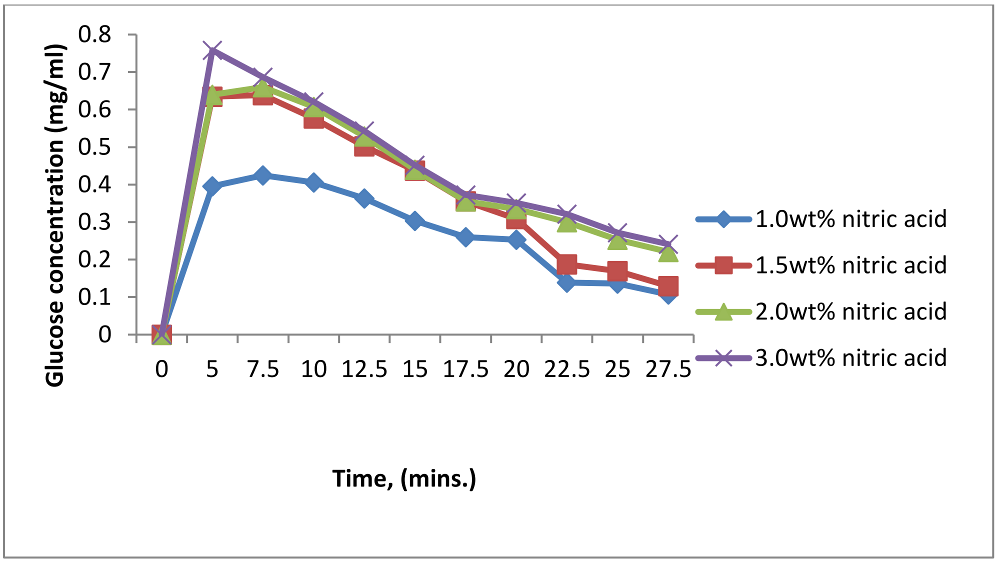


Fig. 2: Glucose yield obtained from cassava peel

3.2.2 Reaction kinetics and modeling of glucose production

Figure 2 shows that there is both production and degradation of glucose therefore two steps irreversible series reaction is involved according to Eq. (1).

Cassava peel $\overset{k_1}{\rightarrow}$ Glucose $\overset{k_2}{\rightarrow}$ Degradation product (1)

According to Fig. 1, cassava peel comprises of cellulose, hemicellulose, lignin and other composition. Cellulosic fraction majorly produces glucose and the hemicellulosic fraction produces xylose. Therefore Eq. (1) can be modified to give Eq. (2).

Cellulose (A) $\overset{k_1}{\rightarrow}$ Glucose (G) $\overset{k_2}{\rightarrow}$ Degradation product (D) (2)

The rate of production and degradation of glucose is given by Eq. (3) which can be solved to give Eq. (4).

$$-r_G = -\frac{dC_G}{dt} = k_2 C_G - k_1 C_A \quad (3)$$

$$C_{G(t)} = \frac{k_1 C_{AO}}{(k_2 - k_1)}(e^{-k_1 t} - e^{-k_2 t}) \quad (4)$$

$C_{G(t)}$ is the concentration of glucose at any time and C_{AO} is the initial concentration of the cellulose and it can be determine analytically by Eq. (5) which is called Seaman's model. It was applied by applied by Seaman for the hydrolysis of the cellulose to yield glucose in the sulphuric acid hydrolysis of Douglas fire wood [15].

$$C_{AO} = \frac{Fz\rho}{LSR} \quad (5)$$

F is the stoichiometric factor due to hydration of molecule during the hydrolysis (180/162), ρ is the density of the hydrolysate (1510 mg/ml), z is the composition of the raw material from the polysaccharides (3.05 %) and LSR is liquor to solid ratio that is 5g of cassava peel to 50 ml nitric acid (15.1). In this research work C_{AO} was calculated as 3.3889 mg/ml, thus the Seaman's model can be written as Eq. (6).

$$C_{G(t)} = \frac{3.3889 k_1}{(k_2 - k_1)}(e^{-k_1 t} - e^{-k_2 t}) \quad (6)$$

The Two-fraction model is based on the idea that only a fraction of the lignocellulosic material reacted (fast hydrolysed fraction) and the fraction that does not react is called the slow fraction. The ratio of fast fraction to the total fraction is given by parameter α which must be less than or equal to one (1) [8]. The two-fraction model of this work is given by Eq. (7)

$$C_{G(t)}=\frac{3.3889k_1\alpha}{(k_2-k_1)}\left(e^{-k_1 t}-e^{-k_2 t}\right) \tag{7}$$

The Experimental data were fit with MATLAB 7.5.0 into Eq. (6) and (7) to obtain k_1, k_2, R^2 and adjusted R^2.The results of these fits are given by Fig. 3, Table 1 and Table 2.

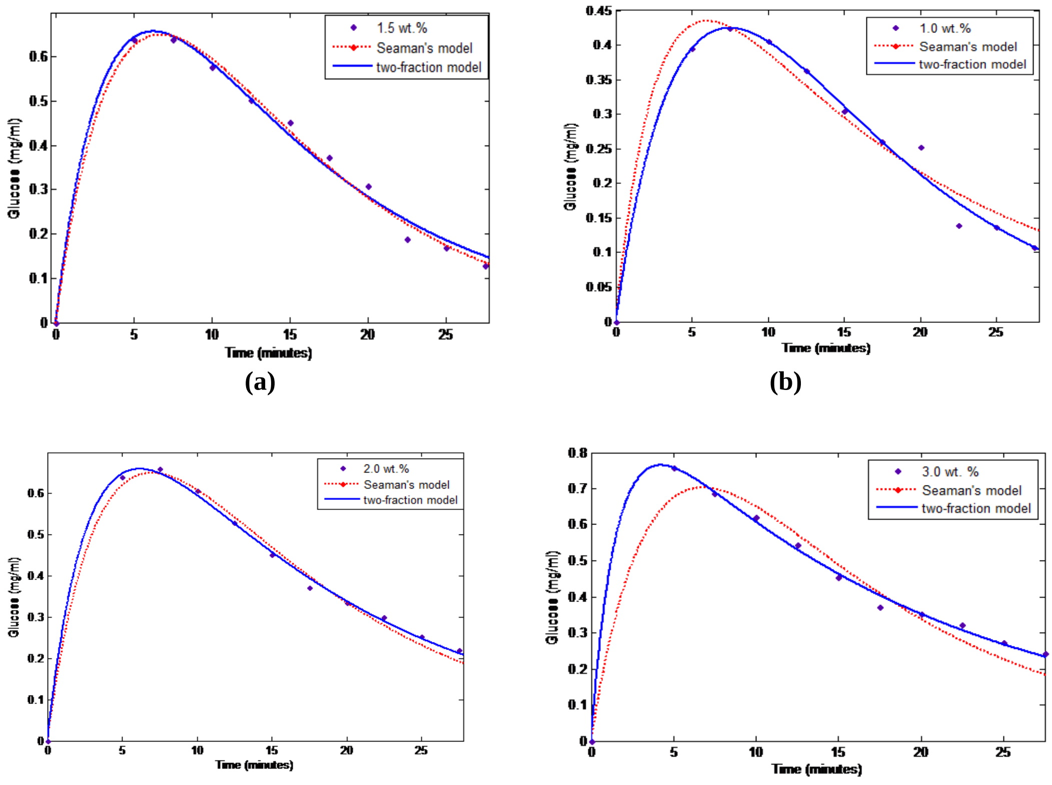


Fig. 3a-d: Experimental and predicted model graphs for glucose concentration at different nitric acid concentration.

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

Concentration	$k_1(min^{-1})$	$k_2(min^{-1})$	R^2	**Adjusted R^2**
1.0	0.06451	0.3412	0.9671	0.9624
1.5	0.08898	0.2655	0.9927	0.9919
2.0	0.07897	0.2387	0.9878	0.9865
3.0	0.08624	0.2315	0.9611	0.9598

Table 2: Kinetic parameters obtained from Two-fraction model for glucose production

Concentration	$k_1(min^{-1})$	$k_2(min^{-1})$	α	R^2	**Adjusted R^2**
1.0	0.1334	0.1338	0.3411	0.9863	0.9829
1.5	0.2012	0.1092	0.3947	0.9945	0.9931
2.0	0.344	0.06271	0.2846	0.9945	0.9931
3.0	0.633	0.0549	0.2846	0.9964	0.9955

Comparing the two models, it was observed that two-fraction model gave a better fit because the adjusted R^2 values obtained in this model are greater than those obtained from the Seaman's model. Aguilar et al. [16] studied the kinetics of acid hydrolysis of sugar cane bagasse and they reported that two fraction model also gave a better fit to the data obtained. From Table 2 it was observed that the rate of glucose production (k_1) increased with increase in acid concentration. Also α obtained varied from 0.2846 to 0.3411, with an average value of

0.3263. With 1.0 wt. % nitric acid k_2 was greater than k_1 and this shows that the rate of degradation was greater than the rate of generation while with 1.5, 2.0 and 3.0 wt. % the rate of generation was greater than the rate of degradation. Substituting α, k_1 and k_2 from Table 2 into Eq. (7) one can predict the concentration of glucose obtainable at these different concentration of nitric acid.

3.3 The study of xylose production

3.3.1. Effect of acid concentration and time variation on xylose yield

Fig. 4 shows xylose yield obtained from cassava peel hydrolyzed with 1.0 wt. %. 1.5 wt. %, 2.0 wt. % and 3.0wt.% nitric acid. Using 1.0 wt. %, the xylose yield increased very rapidly for the first 5 minutes and increased slightly for the next 5 minutes where it maintain a constant concentration of 0.5127 mg/ml for the next 2.5 minutes and it began to decrease slightly. 1.5 wt. %, 2.0 wt. % and 3.0 wt. % follow similar trend with 1.0 wt. % where they have maximum yield of 0.5345 mg/ml at 10 minutes, 0.6909 mg/ml at 7.5 minutes and 0.9091 mg/ml at 7.5 minutes respectively. From Fig. 4, it was observed that xylose yield increases with an increase in acid concentration. The decrease in xylose yield can be associated with the degradation reaction of xylose.

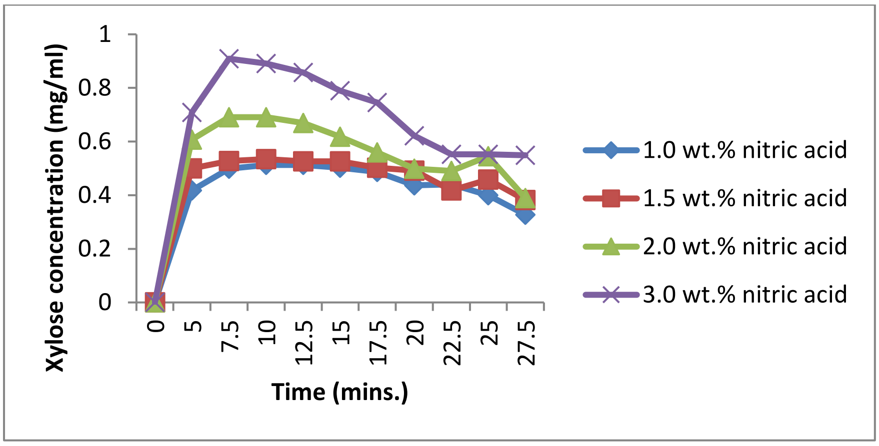


Fig 4: Xylose yield obtained from cassava peel

3.3.2. Reaction kinetics and modeling of xylose production

The rate of production and degradation of glucose is given by Eq. (8) which can be solved to give Eq. (9).

Hemicellulose (B) $\overset{k_1}{\rightarrow}$ Xylose (X) $\overset{k_2}{\rightarrow}$ Degradation product (S) (8)

$$C_{X(t)}=\frac{k_1 C_{BO}}{(k_2-k_1)}\left(e^{-k_1 t}-e^{-k_2 t}\right) \quad (9)$$

C_{BO} is the initial concentration of the hemicellulose and it can be determine analytically by Eq. (10).

$$C_{BO}=\frac{Fz\rho}{LSR} \quad (10)$$

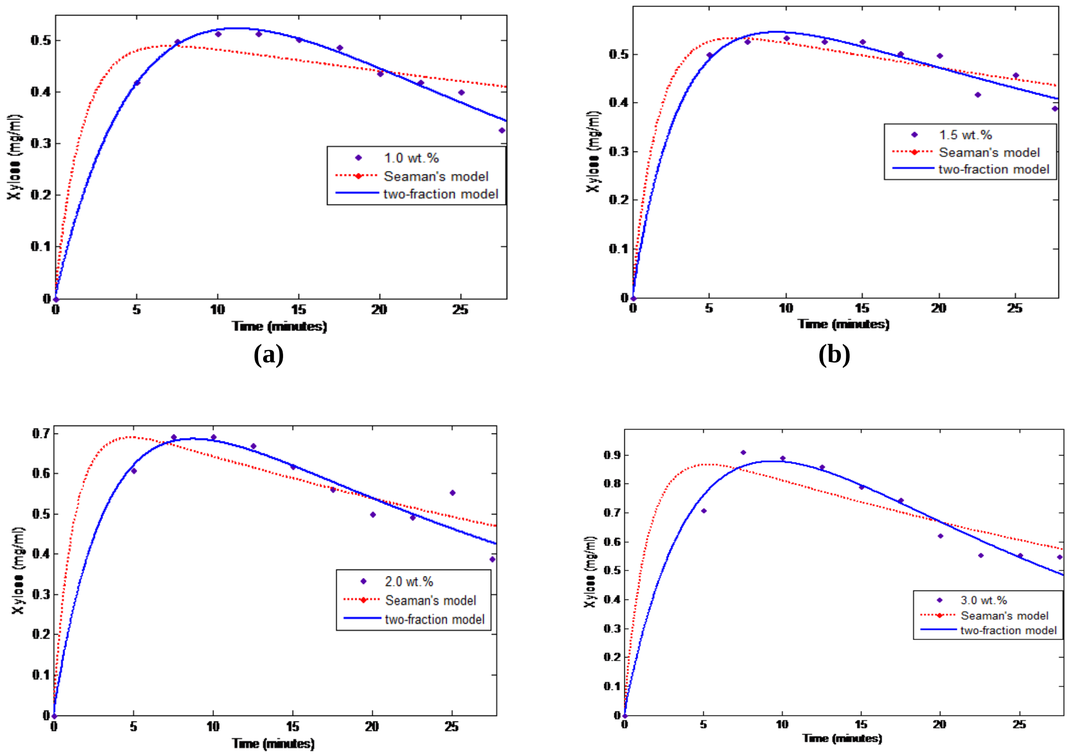
ρ and LSR values are the same with glucose. F =150/132, z = 29.81 %

Therefore C_{BO} was calculated to be 33.8761 mg/ml and substituted into Eq. (9) to obtain Eq. (11) and (12) as Seaman's model and two-fraction model respectively for xylose production.

$$C_{X(t)}=\frac{33.8761 k_1}{(k_2-k_1)}\left(e^{-k_1 t}-e^{-k_2 t}\right) \quad (11)$$

$$C_{X(t)}=\frac{3.3889 k_1 \alpha}{(k_2-k_1)}\left(e^{-k_1 t}-e^{-k_2 t}\right) \quad (12)$$

The Experimental data were fit with MATLAB 7.5.0 into Eq. (11) and Eq.(12) to obtain k_1, k_2, R^2 and adjusted R^2 .The result of the fit obtained are shown in Fig. 5a-d., Table 3 and Table 4.



(a) (b) (c) (d)

Fig. 5a-d. Experimental and predicted models at different concentration of nitric acid

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

Concentration	$k_1(min^{-1})$	$k_2(min^{-1})$	R^2	Adjusted R^2
1.0	0.008711	0.5671	0.9231	0.9145
1.5	0.01077	0.6372	0.9692	0.9657
2.0	0.018	0.8104	0.9359	0.9288
3.0	0.01966	0.6931	0.9099	0.8999

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

Concentration	$k_1(min^{-1})$	$k_2(min^{-1})$	α	R^2	Adjusted R^2
1.0	0.03866	0.1696	0.1049	0.9916	0.9895
1.5	0.02005	0.3112	0.3021	0.9853	0.9816
2.0	0.2796	0.03178	0.02676	0.9717	0.9647
3.0	0.04517	0.2066	0.1813	0.9786	0.9732

Comparing adjusted R^2 values of Table 3 with that of Table 4, it can be observed that the two-fraction model gave a better prediction than the Seaman's model. This result is in agreement with result obtained by Rodrıguez-Chong [17]. The value of α obtained was between 0.02676 and 0.3021. Furthermore the rate of generation was greater than the rate of degradation only with 2.0 wt. % nitric acid while the rate degradation was greater than the rate of generation with 1.0 wt. %, 1.5 wt. % and 3.0 wt. % nitric acid according to Table 4. Substituting α, k_1 and k_2 from Table 4 into Eq. (12) one can predict the concentration of xylose at different concentration of nitric acid.

IV. CONCLUSION

Based on the results obtained it can be concluded that cassava peel can be hydrolyzed with nitric acid at different concentration to obtain glucose and xylose. Predictions can also be made on the yield of these sugars at these concentrations and temperature studied using two-fraction model.

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