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OPTIMIZATION OF ACID HYDROLYSIS OF MIXED PEELS TO GLUCOSE

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ABSTRACT

The optimization of glucose production via acid hydrolysis of mixed peels was carried out. The substrate was characterized using proximate analysis. The process was optimized using response surface methodology while the experimental data were subjected to power rate law for kinetics study. The results obtained showed that the mixed peels have high hemicellulose content, hydrolysable carbohydrate and cellulose. The optimum conditions for obtaining of glucose yield via acid hydrolysis (36.17 %) are temperature 40^{o}C, reaction time 31 minutes, and acid concentration 2.15 M. It was observed that acid hydrolysis obeyed power law model with rate constant of 6.41 x 10^{-3} L $g^{-1}min^{-1}$, reaction order of approximately 2 and the reaction was feasible. Therefore, the results have proved that mixed cassava and potato peels can serve as substrate for glucose production via acid hydrolysis.

Keywords: *acid hydrolysis, optimization, glucose, cassava and potato peels.*

INTRODUCTION

The environmental challenges associated with the use of petroleum fractions have generated great concern for an alternative energy sources that are environmentally friendly [1]. Biofuels like biodiesel, bioethanol and biogas are energy sources that have attracted the interest of researchers. Nigeria hopes to have a good percentage blending of biofuels in the national liquid fuel supply in nearest future to supplement our crude oil and cub environmental problems. Development of glucose which is a primary source of bioethanol in Nigeria will help to record success in pursuit of alternative source of energy.

The use of starchy food as feed stocks for glucose production in Nigeria will compete with the food chain and make the cost of bioethanol expensive. An alternative feed stock from waste/peels thus needs to be found to produce an affordable bioethanol for economic empowerment. The production of glucose from lignocellulosic biomass like mixture of cassava and potato peels is better choice than starch and sugar crops because of the comparative accessibility agricultural, and other cellulosic resources which do not compete with existing food chain [2]. In addition, converting these peels into valuable product like glucose and ethanol provides a potential alternative for treatment and disposal of such materials. Moreover, the conversion of waste lignocelluloses and lignocelluloses materials to glucose will lead to diversification of economy, reduce unemployment and clean environment without altering human food chain [3]. The uses of mixture of different lignocelluloses materials to ensure production of glucose for bio-ethanol production that will be sufficient for commercial purpose are yet to be explored. Therefore, this paper focused on synthesis of glucose as a starting substrate for further bioethanol production from mixture of cassava and potato peels via acid hydrolysis. In addition, optimization of the process and kinetics is done.

EXPERIMENTAL

Materials

Cassava and potato peels were collected from Abakaliki, Ebonyi State. The sulfuric acid (H_2SO_4) was purchased from Ogbete Main Market, Enugu, Enugu State, Nigeria.

Methods

Characterization

The peels were adequately washed with clean water and dried under sunlight for 5 days. They were mixed in a ratio of 50:50 wt/wt, then grounded with a grinding machine and sieved to particle size of 0.3 mm. Onyelucheya and Viruthajru technique was used in measuring the cellulose and hemicellulose compositions of the sample [4]. Also, the method of Ana et al. was adopted in determining lignin content of the sample with little modification [5].

Acid hydrolysis

20 g of the sample was mixed with 1000 mL of 0.2 M H_2SO_4 in a 2000 mL flat bottom flask. The mixture was placed in an autoclave and heated to 40^{o}C for 10 min. Then it was sieved and transferred to an ice bath to quench the reaction. The glucose concentration of the filtrate was determined using 3,5-dinitrosalicylic acid method employed by Onyelucheya and Viruthajru at the absorbance of 540 nm [4]. The procedure was repeated with 40, 60, 80 and 100 g L^{-1} glucose for 20, 30, 40 and 50 min at 50, 60, 70 and 80^{o}C. Acid concentration was also varied at 0.4, 0.6, 0.8 and 1 M, respectively.

Central composite design (CCD) of experiment for acid hydrolysis

The central composite design (CCD) of response surface methodology (RSM) of Design Expert software version 10 was used to design the experiment and to optimize the process parameters for the acid hydrolysis of the mixed peel to glucose. A two-level-four factor full factorial design consisting 30 experiments was used for the analysis. Temperature, reaction time, substrate dosage and acid concentration are selected as independent factors for the optimization study. The response chosen was the glucose yield obtained from acid hydrolysis of cellulose. Six replications of center points were used in order to predict a good estimation of errors and experiments were performed in a randomized order. The actual and coded levels of each factor are shown in Table 1.

The design matrix is shown in Table 2.

Kinetic Modeling of the acid Hydrolysis of mixed peels

The kinetics model was developed using power rate law as given in equation (1) and it was used to study the kinetics of acid hydrolysis.

$$r_s = -\frac{dC_s}{dt} = kC_s^{\alpha} \tag{1}$$

Therefore, k and α are the kinetic parameters to be determined. Taking the natural logarithm of both sides of equation (1) it becomes equation (2):

$$\ln r_s = \ln k + \alpha \ln C_s \tag{2}$$

where C_s is the concentration of the substrate, r_s is the rate of consumption of the substrate, k is the rate constant and α is the reaction order.

The order of the reaction and rate constant can be deduced from the plot of $\ln r_s$ vs. $\ln C_s$.

The numerical technique can be used to estimate the rate, $\frac{dC_s}{dt}$ because the independent variables are varied at equal intervals [6]. The three point-differential formula was applied in this work. Typically, the tabulation of the

Table 1. Studied range of each factor in actual and coded form for acid hydrolysis of glucose.

Factor	Units	Low level	High level	-α	+α	0 level
Temperature (A)	°C	50(-1)	70(+1)	40(-2)	80(+2)	60
Time, (B)	minutes	20(-1)	40(+1)	10(-2)	50(+2)	30
Substrate dosage (C)	g L^{-1}	40	80	20	100	60
Acid concentration (D)	(mol dm^{-3})	0.4(-1)	0.8(+1)	0.2(-2)	1.0(+2)	0.6

Table 2. Experimental design matrix for acid hydrolysis of glucose.

Run order	Temperature, °C A		Time, minutes B		Substrate dosage, g L^{-1} C		Acid concentration (molar) D		Glucose conc. from mixed peel
	Coded	Real	Coded	Real	Coded	Real	Real	Coded	%
1	-1	50	-1	20	-1	40	-1	0.4	50
2	+1	70	-1	20	-1	40	-1	0.4	50
3	-1	50	+1	40	-1	40	-1	0.4	55
4	+1	70	+1	40	-1	40	-1	0.4	50
5	-1	50	-1	20	+1	80	-1	0.4	41
6	+1	70	-1	20	+1	80	-1	0.4	45
7	-1	50	+1	40	+1	80	-1	0.4	48
8	+1	70	+1	40	+1	80	-1	0.4	51
9	-1	50	-1	20	-1	40	+1	0.8	47
10	+1	70	-1	20	-1	40	+1	0.8	50
11	-1	50	+1	40	-1	40	+1	0.8	49
12	+1	70	+1	40	-1	40	+1	0.8	43
13	-1	50	-1	20	+1	80	+1	0.8	46
14	+1	70	-1	20	+1	80	+1	0.8	50
15	-1	50	+1	40	+1	80	+1	0.8	52
16	+1	70	+1	40	+1	80	+1	0.8	45
17	-2	40	0	30	0	60	0	0.6	44
18	+2	80	0	30	0	60	0	0.6	48
19	0	60	-2	10	0	60	0	0.6	51
20	0	60	+2	50	0	60	0	0.6	39
21	0	60	0	30	-2	20	0	0.6	46
22	0	60	0	30	+2	100	0	0.6	40
23	0	60	0	30	0	60	-2	0.2	37
24	0	60	0	30	0	60	+2	1.0	39
25	0	60	0	30	0	60	0	0.6	55
26	0	60	0	30	0	60	0	0.6	56
27	0	60	0	30	0	60	0	0.6	58
28	0	60	0	30	0	60	0	0.6	60
29	0	60	0	30	0	60	0	0.6	59
30	0	60	0	30	0	60	0	0.6	58

concentration variation with time is as shown in Table 3.

The three-point differential formulae are presented in equations (3) to (5):

Initial point:

$$\left(\frac{dC_s}{dt}\right)_{t_0} = \frac{C_{s0} + C_{s1} - C_{s2}}{2\,\Delta t} \tag{3}$$

Interior point:

$$\left(\frac{dC_s}{dt}\right)_{t_1} = \frac{C_{s2} - C_{s0}}{2\Delta t} \tag{4}$$

Last point:

$$\left(\frac{dC_s}{dt}\right)_{t_0} = \frac{C_{s3} - 4C_{s4} + 3C_{s5}}{2\Delta t} \tag{5}$$

Equations (3) to (5) were used to calculate the change in the reaction concentration with time $\frac{dC_A}{dt}$. The procedure of Nitayavardhana et al. was used to determine the concentration of substrates cellulose and hemicellulose [7]. The amount of cellulose and hemicellulose was measured by dissolving other components of the peel. 57.4 g of the sample was mixed with 1000 mL of 0.615 M of H_2SO_4 in a 2000 mL round bottom flask fitted with a reflux condenser. The flask was placed on a heating mantle and the mixture was heated for 0.5 hours and filtered. The residue is washed and dried in an oven at 105˚C for 1 hour. The dried residue was weighed as the cellulose and hemicellulose content of the sample (Table 3).

Table 3. Tabulation of the concentration variation with time.

Time (hrs)	t_0	t_1	t_2	t_3	t_4	t_5
C_s,(g dm^{-3})	C_{s0}	C_{s1}	C_{s2}	C_{s3}	C_{s4}	C_{s5}

RESULTS AND DISCUSSION

Characterization of substrate

Table 4 shows the proximate composition of the mixed peels. The sample was observed to have relatively low moisture content of 0.42 %. The proximate analysis of the mixed peel shows that it contains high percentage of hydrolysable carbohydrate and cellulose. This implies that the mixed peel is a good substrate for glucose production which will be converted to bio-ethanol.

Statistical analysis and optimization of acid hydrolysis of mixed peels

The empirical relationship between yields of glucose produced (Y) and the three variables in coded values obtained by using the statistical package Design-Expert 10 version for determining the levels of factors which gives optimum glucose yield was given by the equation below. A quadratic regression equation that fitted the data after the removal of the insignificant terms is started in equation (6):

$$Y = 50.67 + 0.25A - 0.49B - 1.25C + 0.65D + 0.74AB + 2.13BC + 1.74BD - 0.88CD - 3.77A^2 - 3.91B^2 - 4.39C^2 - 4.12D^2 \tag{6}$$

Table 4. Proximate analysis of mixed peels.

S/N	Proximate Analysis	Composition before treatment (%)	Composition after treatment (%)
1	Protein	5.43	0.96
2	Ash	3.89	4.35
3	Fibre	1.28	1.32
4	Lipid	2.04	0.22
5	Moisture	0.41	0.38
6	Carbohydrate	86.95	92.77
7	Cellulose	32.10	34.70
8	Hemicellulose	39.23	39.48
9	Lignin	15.19	15.19
10	Extractive	5.23	6.74

Optimization Result

The glucose yield was optimized with the design expert giving a 50.82 % of glucose at optimum conditions of temperature 60°C, reaction time 29.6 min, substrate concentration 57.4 g L^{-1} and acid concentration 0.615 M with desirability of 0.949. The optimum conditions were used to produce glucose in order to validate the quadratic model. The experimental value and predicted values are shown in Table 5. Comparing the results, less than 1 % error was recorded therefore concluding that the generated model can accurately predict the glucose production via acid hydrolysis.

Kinetics and thermodynamics of acid hydrolysis

The kinetic plot is presented in Fig. 1 and the values of k and α were determined to be 1.66 x 10^{-2} dm^3g^{-1} min s^{-1} and 1.9, respectively. The order of reaction α is approximately 2, which shows that the reaction is of the second order.

Based on the kinetic values presented in Table 6, the kinetic equation for acid hydrolysis is given in equation (7). Negative ΔG obtained shows that acid hydrolysis of mixed peel cellulose is feasible. The lower negative value of ΔG for acid hydrolysis shows that the hydrolysis is highly feasible suggesting rapid spontaneous disintegration of the substrate into the product [8, 9].

$$-r_s = 0.0166 C_s^{1.9} \quad (7)$$

CONCLUSIONS

The results obtained in this study have shown that combination of cassava and potato peels is a good quantity of hydrolysable cellulose that can be hydrolyzed by acid**.** The optimum conditions for glucose yield of 51 % by acid hydrolysis are temperature 60°C, reaction time 29.6 min, substrate concentration 57.4 g L^{-1} and acid concentration 0.615 M. Acid hydrolysis obeyed power law model.

Table 5. Results of the model validation (experiment to validate the optimum glucose production by acid hydrolysis of cellulose).

Experiment	Temperature, °C A	Time, minutes B	Substrate concentration, g L^{-1}	Acid concentration, M	Experimented glucose yield, %	Predicted glucose yield, %	% Error
1	60	29.6	57.4	0.615	50.83	51.0	0.33

Table 6. Kinetic and thermodynamic parameters for acid hydrolysis.

K, g dm^{-3} min^{-1}	α	R^2	ΔG (kJ/mol)
0.0166	1.9	0.95	-0.084

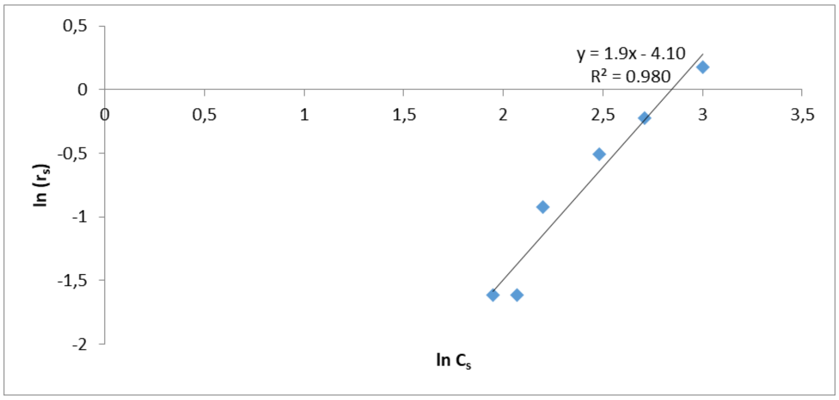

Fig. 1. Plot of ln r_s versus ln C_s.

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