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Kinetic Study of Dilute Acid Hydrolysis of Cowpea Seed Husk for Production of Glucose

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Authors' contributions

This work was carried out in collaboration among all authors. Authors MEO and NJT designed the study, performed the statistical analysis and wrote the first draft of the manuscript. Authors MEO, OCE and ICEU managed the analyses of the study. All authors read and approved the final manuscript

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ABSTRACT

Acid hydrolysis of Cowpea seed husk was carried out using sulphuric acid with the concentrations of 0.1 M and 0.5 M at a reaction time of 10 to 90 minutes and temperatures of 130ºC to 170ºC. The substrates were characterised using proximate analysis. The effects of process parameters that were studied on glucose yield were; time, temperature, substrate concentration, and acid concentration. The experimental data obtained for glucose yield were fitted into the Saeman's model and Two –fraction models. The result obtained from the proximate analysis shows that cowpea seed husk has a cellulose content of 31.7%, hemicelluloses of 26.7% and lignin 6.1%. The maximum glucose yield of 27.1% was obtained at temperature of 150ºC, a reaction time of 50 minutes, 0.02 g/ml substrate concentration, and 0.5 M acid concentration. The two-fraction model gave a better fit of the experimental data over saeman's model. From the study it is concluded that cowpea seed husk can be a good source for glucose production.

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Keywords: *Acid hydrolysis; cowpea seed husk; kinetics parameters; glucose concentration; seaman model; two-fraction model.*

1. INTRODUCTION

Over the last few decades, the negative impacts of fossil fuel on the environment and consequooent global warming, progressive demand for energy, inevitable depletion of the world's energy supply, and the unstable oil market have renewed the interest of society in searching for alternative fuels. The alternative fuels are expected to satisfy several requirements including substantial reduction of greenhouse emission, world wide availability of raw materials, and capability of being produced from renewed feedstock such as agricultural waste [1]. Agricultural activities of man have resulted in the production of large quantities of waste biomass that tends to dominate and pollute the environment. Many of these agricultural wastes such as cowpea seed husk are allowed to rot away unutilised [2]. According to IITA [3], more than 5.4 million tons of dried cowpeas are produced worldwide with African producing nearly 5.2 million. They also reported that Nigeria is the largest producer and consumer of cowpea, accounting for 61% of production in Africa. In order to obtain the cowpea seed, it is dehusked, thereby generating large quantities of husks as wastes to our environment. These husks generated are highly fibrous. The biomass wastes comprises of cellulose, hemicelluloses, lignin and other components also known as extractives [4,5]. Among all these constituents of agricultural wastes biomass, cellulose is the main structural constituents in plant cell walls. The cellulose can be hydrolysed to produce glucose which can further be fermented to produce ethanol [4,5]. Hemicelluloses and cellulose are usually hydrolysed with a chemical process (acid) or biological (enzyme) attack. The economic success of ethanol production will depend on efficient conversion of cellulose and hemicelluloses to their monomeric sugar, while also reducing capital and operating cost [6]. For the effective conversion of lignocellulosic into sugar and further to ethanol, there are three major steps in the conversion process, First – A pre-treatment phase which might be physical or chemical, to make the raw material amenable to hydrolysis; Second – Hydrolysis, to break down the molecules of cellulose into their monomeric sugar constituents; Thirdly – fermentation of the released sugars into ethanol by a specialised microorganisms [7]. Cowpea seed husk is produced in enormous quantities by farmers and the economical disposal of them is a serious problem to the country. Therefore, this research work focused on the conversion of cowpea seed husk to liquid glucose using two acid concentrations, three substrate concentrations at different temperatures and different reaction time.

2. MATERIALS AND METHODS

Cowpea seed husk (CSH) used in this study was collected from Ochanja market in Onitsha south local government Area of Anambra State, Nigeria. The husks were collected from the market after they have been dehusked from the seed. It was threshed to remove sand and unwanted materials, and then it was sundried to reduce the moisture contents, milled so as to increase the surface area. It was also screened with a mesh of 0.1 mm diameter and stored for subsequent use.

2.1 Characterisation of the Substrate using Proximate Analysis

Proximate analysis was carried out to determine the percentage composition of the cellulose, hemicelluloses, lignin and other extractives. The cellulose was determined according to method of Onyelucheya, et al. [8] and hemicellulose was determined by sequential chemical extraction according to the method of Sridevi, et al. [9]. Lignin, moisture and ash content were determined using standard methods for proximate analysis according to AOAC [10]. Other extractives were also determined using the method of ethanol extraction in soxhlet extraction apparatus according to Amenaghawon, et al. [11]. The hydrolysis process was carried out according to the method of Joseph, et al. [5].

2.2 Acid Hydrolysis

One gram of the substrate was dissolved in a 50ml of acid solution which is 0.02 g/ml. The solution was placed in a thermal oven at temperature of 130ºC. Samples were drawn at intervals of 20 min for 1.5 hrs. Each sample was placed in a cold water bath to stop the reaction process, the sample was then filtered and the hydrolysate obtained was analysed for its glucose concentration. The glucose concentration of the filtrate was measured using DNS (3, 5- Di nitro salicylic acid) method at the absorbance of 540 nm. The process was repeated for temperatures of 140ºC, 150ºC, 160ºC and 170ºC and substrate concentration of 0.01 g/ml and 0.03 g/ml. Acid concentration of 0.1 M and 0.5 M were used for the sulphuric acid.

2.3 Kinetic Model

Saeman's model, [12] and two-fraction model were used to fit the experimental data and the reaction equation was shown in equation 1

$$\text{Cellulose+water} \xrightarrow{K1} \text{glucose} \xrightarrow{K2} \text{decomposition product} \quad (1)$$

Where K_1 is the rate of conversion of cellulose to glucose and K_2 is the rate of decomposition of glucose. Both K_1 and K_2 have a unit of reciprocal of time (min^{-1}). The reactions are considered to be first order and irreversible. Assuming homogeneous first –order reactions with excess water and integrating equation 1 gives equation 2 [5]

$$G = \left(\frac{k_i C_0}{k_2 - k_1}\right) \left(e^{-k_1}t - e^{-k_2}t\right) + G_0 e^{-k_2}t \quad (2)$$

Where C_0 the initial cellulose concentration, (gL^{-1}); G_0 is the initial glucose concentration (gL^{-1}). Assuming that the initial glucose concentration to be approximately equal to 0 [5], then Eq. (2) become,

$$G = \left(\frac{K_1 C_0}{K_2 - K_1}\right) \left(e^{-K_1 t} - e^{-K_2 t}\right) \quad (3)$$

It is assumed that all the cellulose hydrolyses to glucose, therefore C_0 the initial cellulose concentration, (gL^{-1}) is equal to the potential concentration of glucose Gn_0 obtainable from the cellulose [13]; [5]. Equation (3) becomes:

$$G = \left(\frac{K_1 G_{n0}}{K_2 - K_1}\right) \left(e^{-K_1 t} - e^{-K_1 t}\right) \quad (4)$$

Amenaghawon, et al. [11] modified the Seaman model by the introduction of α into the Seaman's model. □ 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 5

$$G = \alpha \left(\frac{K_1 G_{n0}}{K_2 - K_1}\right) \left(e^{-K_1 t} - e^{-K_1 t}\right) \quad (5)$$

G_{n0} can be determined analytically as described by Gamez, et al. [14] in equation 6

$$G_{n0} = \frac{Fz\rho}{LSR} \quad (6)$$

Where F is the stoichiometric factor due to hydration of molecule during hydrolysis, z is the composition of the raw material for polysaccharides, ρ is the density of hydrolysate. LSR is the liquid to solid ratio [5]. In this work saeman model and two fraction model were used to fit the data for glucose yield from cowpea seed husk. The rate constant and fractional values were obtained from the models using EXCEL PACKAGE.

The temperature dependence of the reaction rates can be described by Arrhenius equation, equation (7) [5]

$$K_i = K_{i0} e^{-Ea/RT} \quad (7)$$

K_i = kinetic coefficient (i =1 or 2) (min^{-1})
K_{i0} = pre-exponential factor (i 1 or 2) (min^{-1})
Ea = Activation Energy (KJ/mol/k)
R = Gas constant, 8.314 (KJ/mol/k)
T =Temperature (K)

Linearizing equation 7, gives equation (8)

$$\ln k_i = \frac{-Ea}{R}\frac{1}{T} + \ln K_{i0} \quad (8)$$

Plotting lnK versus 1/T allows for the calculation of the activation energy.

3. RESULTS AND DISCUSSION

3.1 Proximate Analysis of Cowpea Seed Husk

The result obtained from the proximate analysis of cowpea seed husk as represented in Table 1 shows a cellulose composition of 31.7%, hemicelluloses 26.7%, lignin 6.1%, ash 9.1%, moisture 6.2%, extractives 20.7%. Amenaghawon, et al. [11] studied sugarcane baggasse and corn stover and recorded 39.5% cellulose, 22.1% hemicelluloses and 17.1% lignin for sugarcane bagasse and recorded 36.1% cellulose, 21.1% hemicelluloses and 17.2% lignin for corn Stover. Adebiyi, et al. [15] Studied the composition of cowpea seed hull and recorded 28% hemicelluloses, 40% cellulose and acid detergent lignin 13%.

3.2 Effects of Time and Temperature on Glucose Yield

Fig. 1 shows the effects of time and temperature on glucose yield from cowpea seed husk hydrolysed with 0.5 M sulphuric acid at temperatures of 130ºC to 170ºC. The glucose yield was observed to increase gradually with an increase in temperature and time until it reached its maximum peak values.

Table 1. Chemical composition of cowpea seed husk before hydrolysis

Components	Cowpea seed husk (% Composition)
Cellulose	31.7
Hemicellulose	26.7
Lignin	6.1
Ash	9.1
Moisture	6.2
Ethanol soluble extractive	4.6
Water soluble extractives	16.1

At 130ºC, a peak value of 25.35% was obtained after 50 minutes of reaction time. However there was a decline in glucose yield even as the time increases. A maximum glucose yield of 26.23% was obtained at 140ºC and at time of 50 minutes. This value obtained at this temperature was slightly higher than that obtained at 130ºC. There was also a decline in glucose yield after 50 minutes. At 150ºC the maximum glucose yield of 27.102% was obtained at 50 minutes after which the glucose yield decreased rapidly. A similar trend was also observed at temperatures of 160ºC and 170ºC with maximum peak values of 25.21% and 23.32% respectively. At 170ºC, it was observed to have attained its maximum yield earlier at 30 minutes than at other temperatures. This implies that at a higher temperature, glucose yield is obtained at a lesser time. Fig. 2 shows the effect of time and temperature on glucose yield from cowpea seed husk hydrolysed with 0.1 m sulphuric acid. For temperatures of 130ºC, 140ºC, 160ºC and 170ºC, the rate of glucose yield was increasing with a longer period of time than at the temperature of 150ºC. The reactions at these temperatures were observed to occur at a reaction time of 70 minutes. It also shows a very small degree of glucose decomposition. A glucose yield of 13.37% was obtained at 130ºC. At 140ºC a glucose yield of 13. 41% was obtained. A maximum glucose yield of 13.76 was obtained at a temperature of 150ºC. At 160ºC, a glucose yield of 13.39% was observed. A glucose yield peak value of 13.30% was obtained at the temperature of 170ºC. From these results it can be observed that increase in temperature and time beyond 150ºC and 50 minutes respectively will reduce the yield of glucose. Similar observation have been reported by several authors [4,16,17,5].

3.3 Effects of Acid Concentration

From Fig. 3, it can be observed that there is a general increase in glucose yield as the time increases for both acid concentrations up till a point where maximum yield was obtained. However there was a decline in glucose yield as the time increases beyond 50 minutes for both acid concentrations. It can be observed from this figure that 0.5 M acid concentration gave a higher yield for glucose than with 0.1 M. This implies that increase in acid concentration increases the yield of glucose. This was also reported by Ajani, et al. [18]. It also agrees with Lenihan, et al. [19].

3.4 Effect of Substrate Concentration on Glucose Yield from Cowpea Seed Husk

Figs. 4 and 5 shows the effect of substrate concentration on glucose yield from cowpea seed husk hydrolysed with 0.1 M and 0.5 M sulphuric acid respectively. From the figures it can be observed that substrate concentration of 0.02 g/ml gave the highest yield of glucose for both acid concentrations. This implies that under the conditions of this research increase in substrate concentration beyond 0.02 g/ml will reduce the yield of glucose. This agrees with [20].

3.5 Kinetic Study

The experimental data obtained for glucose yield were fitted into the saeman and two-fraction models. Tables 2 and 3 shows the kinetic parameters of cowpea seed husk hydrolysed with 0.1 M and 0.5 M sulphuric acid obtained from the saeman and two-fraction models. From the results obtained as shown in Tables 2 and 3, it can be observed that two fraction models gave a better fit than the saeman model. This is based on the values of R^2 obtained with the two fraction model which is higher than those obtained with seaman model. This agrees with Onyelucheya, et al. [8] and Aguilar, et al. [21]. From the two fraction model, the fractional value (□) obtained for 0.1 M acid concentration varies from 0.43 to 0.89 with an average of 0.605 while the fractional value obtained for 0.5 M acid concentration varies from 0.71 to 0.98 with an average of 0.84. From Table 2 the rate of glucose formation increases with temperature using saeman's model while the rate of glucose degradation increases with increase in temperature using two fraction models for 0.1 M sulphuric acid concentration. From Table 3 the rate of glucose formation and degradation increases with temperature for two fraction model while for saeman's model the rate of glucose formation and degradation decreases with an increase in temperature. This shows that increasing the temperature at this condition will reduce the yield of glucose. From Fig. 6, activation energy (E_a) of 8.812 KJ and 8.779 KJ were obtained for K_1 and K_2 respectively for 0.1 M H_2SO_4 acid concentration. This shows that the rate of glucose formation was almost equal the rate of glucose degradation reaction. Activation energy of 13.069 KJ and 41.50 KJ were obtained for K_1 and K_2 respectively for 0.1 M acid concentration as shown in Fig. 7. This shows that the rate of glucose formation reactions will occur earlier than the rate of glucose degradation reaction. From Fig. 8, the activation energy of 3.333 KJ and 20.73 KJ were obtained for K_1 and K_2 respectively for 0.5 M H_2SO_4 acid concentration. This implies that the rate of glucose formation is higher than the rate of glucose degradation. The activation energy of 11.099 KJ and 12.67 KJ were also obtained for K_1 and K_2 respectively for 0.5 M acid concentration as shown in Fig. 9. This also shows that the rate of formation of glucose was higher than the rate of degradation reaction. This agrees with [8] in their study of acid hydrolysis of cassava peel. It also agrees with [19,5].

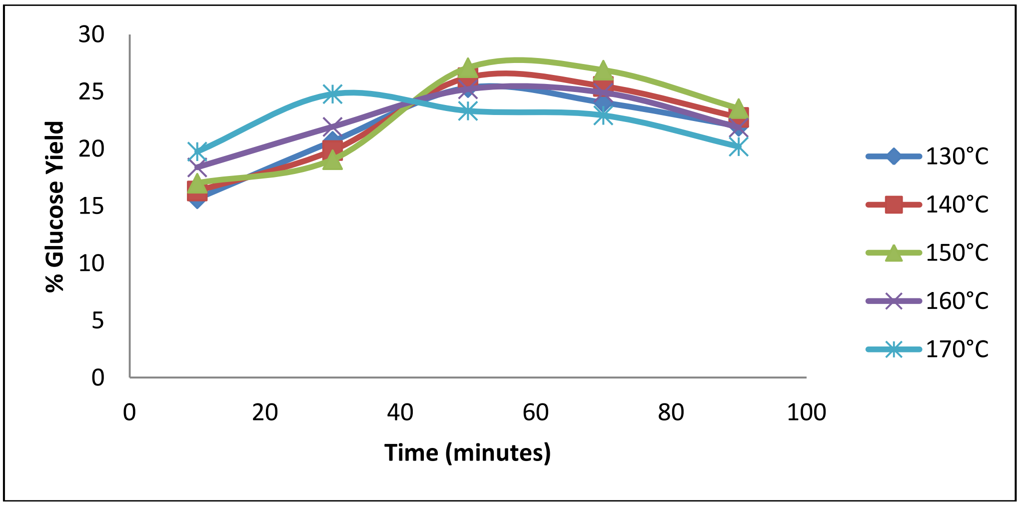

Fig. 1. Effect of time and temperature on glucose yield from cowpea seed husk hydrolysed with 0.5 M sulphuric acid at temperatures of 130°C – 170°C

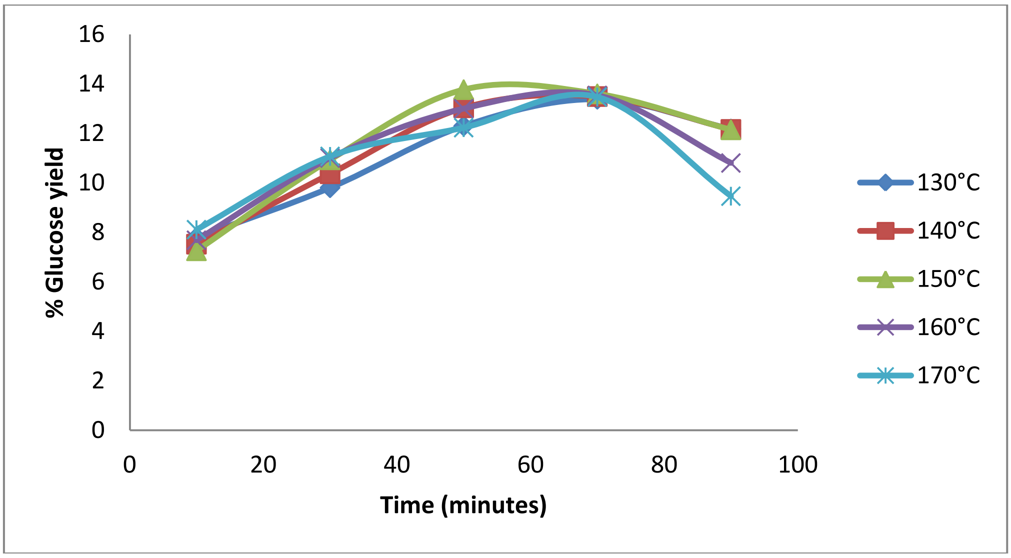

Fig. 2. Effect of time and temperature on glucose yield from cowpea seed husk hydrolysed with 0.1M sulphuric acid at temperatures of 130°C – 170°C

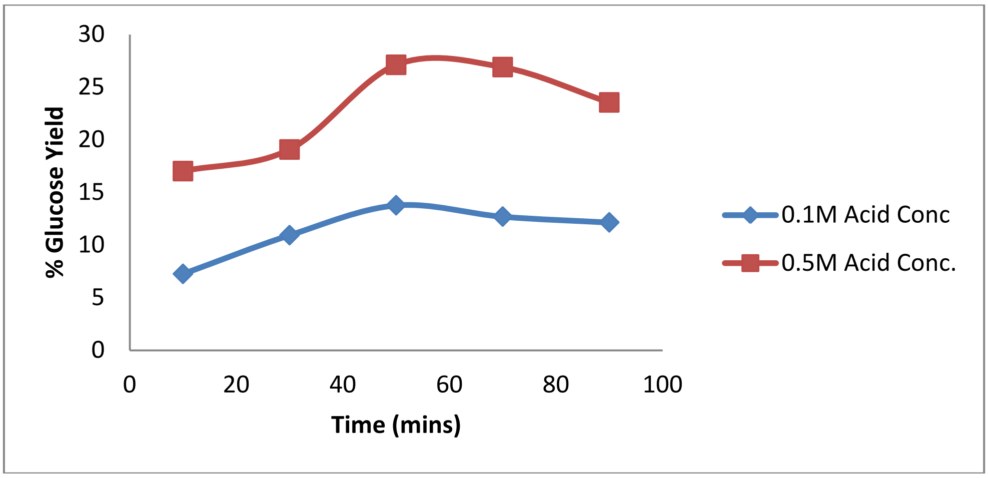

Fig. 3. Effect of acid concentration on glucose yield from cowpea seed husk hydrolyse with sulphuric acid at different temperatures

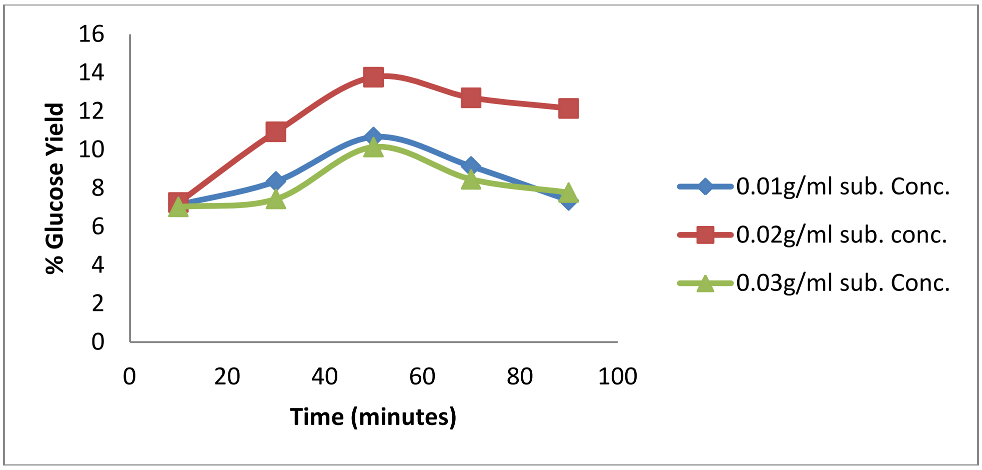

Fig. 4. Effects of substrate concentration on glucose yield from cowpea seed husk hydrolysed with 0.1 M sulphuric acid concentration

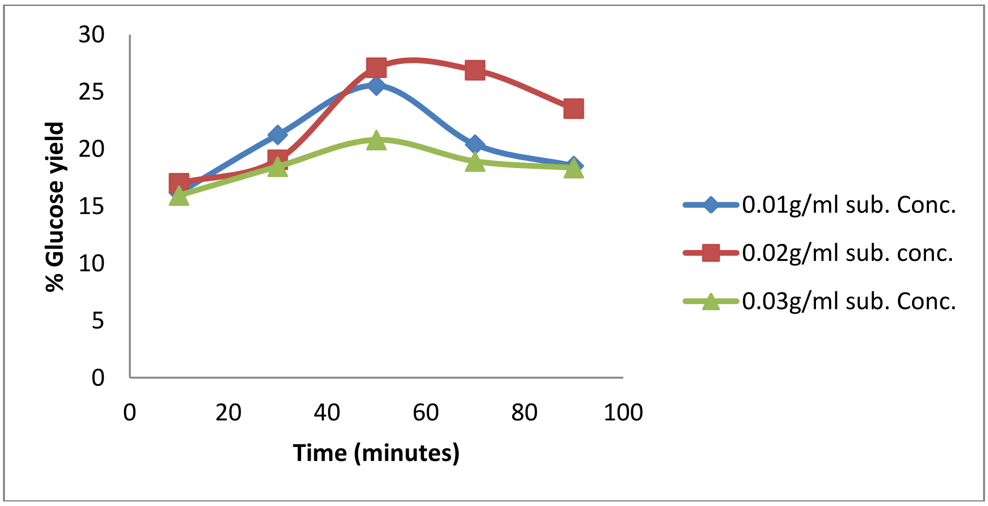

Fig. 5. Effect of substrate concentration on glucose yield from cowpea seed husk hydrolysed with 0.5 M sulphuric acid concentration

Table 2. Kinetic parameters of cowpea seed husk hydrolysed with 0.1 M sulphuric acid concentration

	Seaman's model			Two – Fraction model			
Temp (^{0}C)	**K_1**	**K_2**	**R^2**	**K_1**	**K_2**	□	**R^2**
130	0.0177	0.0166	0.922	0.0716	0.0024	0.7742	0.973
140	0.0188	0.0170	0.903	0.0692	0.0025	0.4286	0.993
150	0.0199	0.0174	0.927	0.0621	0.0035	0.4255	0.927
160	0.0212	0.0192	0.932	0.0589	0.0045	0.5093	0.962
170	0.0225	0.0210	0.673	0.0498	0.0074	0.8872	0.983

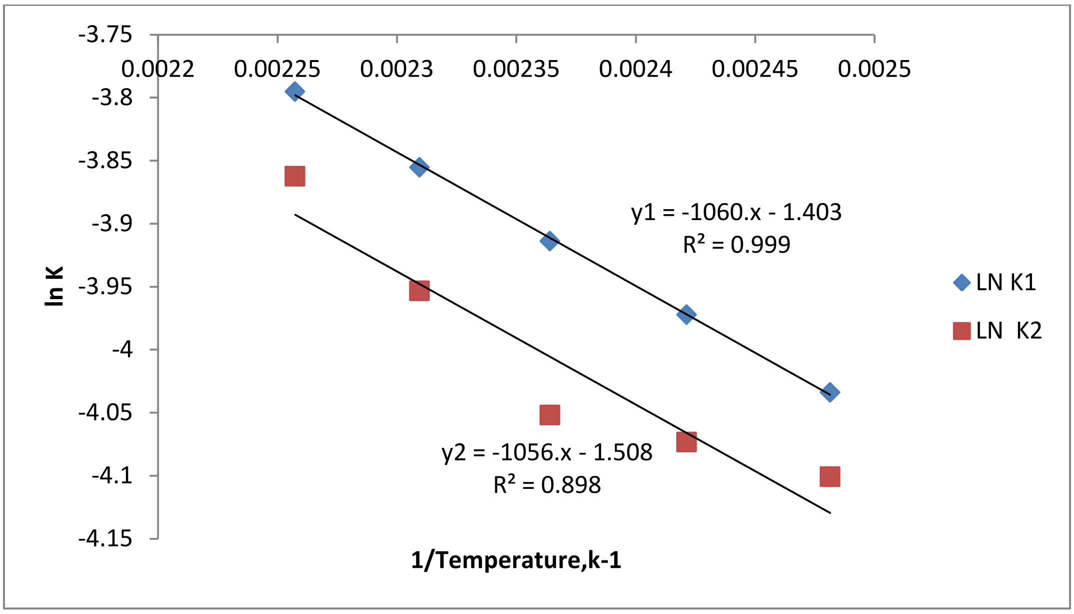

Fig. 6. Arrhenius plot for glucose yield from CSH hydrolysed with 0.1 M H_2SO_4 at 130^{o}C – 170^{o}C using saeman's model

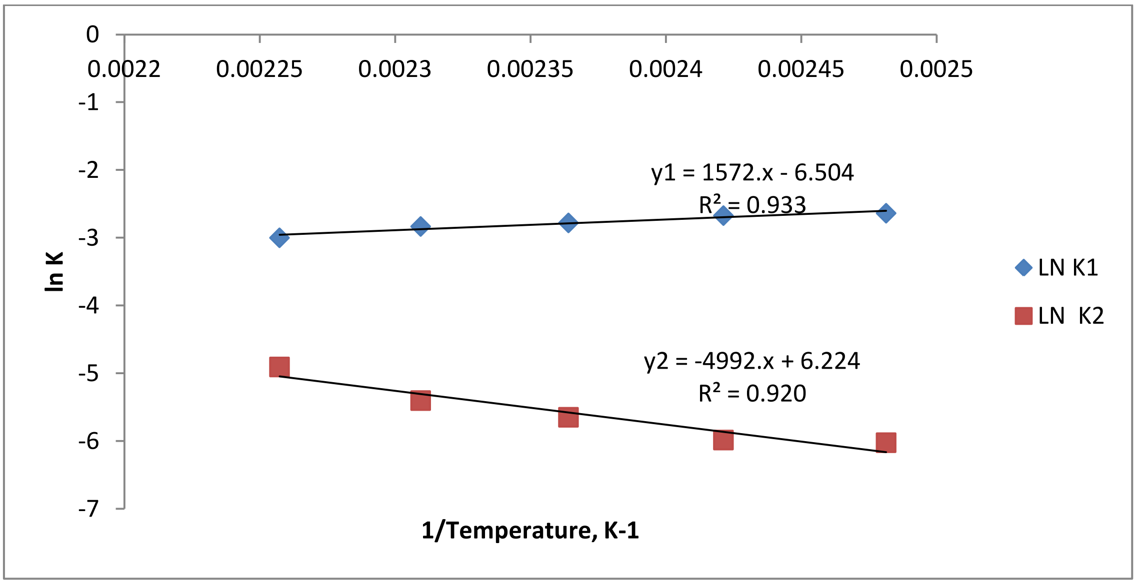

Fig. 7. Arrhenius plot for glucose yield from CSH hydrolysed with 0.1 M H_2SO_4 at 130^{o}C – 170^{o}C using two-fraction models

Table 3. Kinetics parameters of cowpea seed husk hydrolysed with 0.5 M sulphuric acid concentration

	Seaman's model			Two – fraction model			
Temp (^oC)	K_1	K_2	R^2	K_1	K_2	□	R^2
130	0.0484	0.0067	0.936	0.0559	0.0030	0.7163	0.938
140	0.0476	0.0059	0.912	0.0585	0.0034	0.8712	0.984
150	0.0469	0.0051	0.904	0.0682	0.0037	0.9811	0.928
160	0.0457	0.0045	0.834	0.0701	0.0039	0.8653	0.845
170	0.0441	0.0038	0.928	0.0733	0.0044	0.7894	0.936

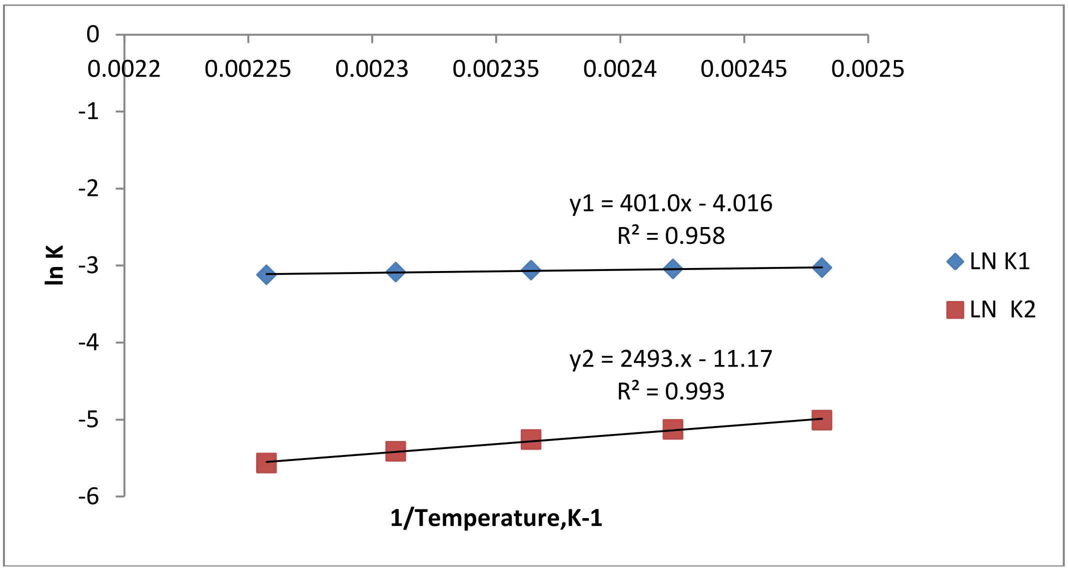

Fig. 8. Arrhenius plot for glucose yield from CSH hydrolysed with 0.5 M H_2SO_4 at 130^oC – 170^oC using saeman's model

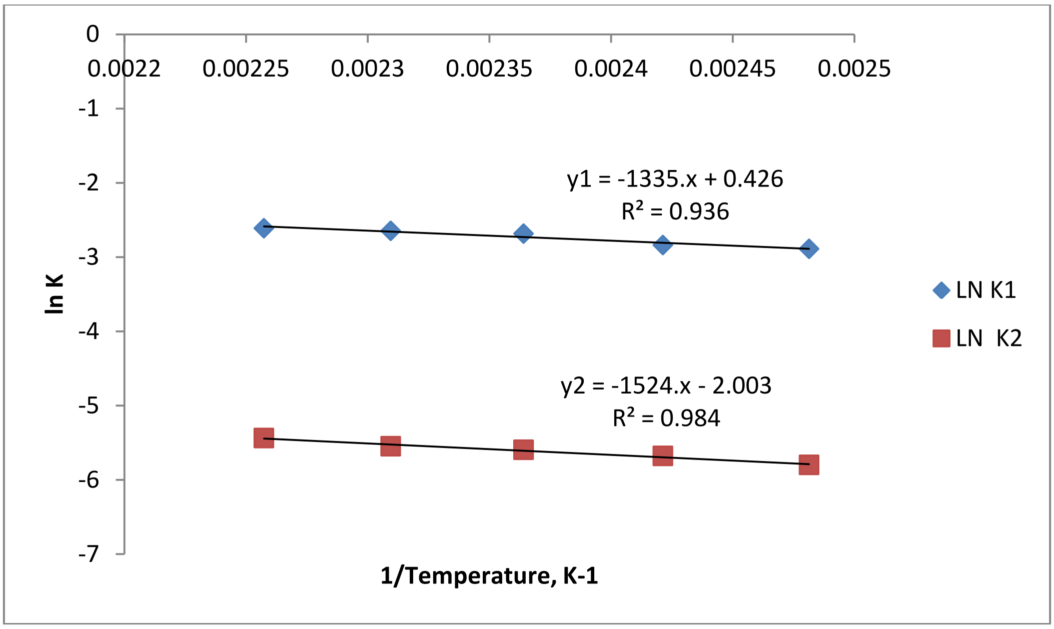

Fig. 9. Arrhenius plot for glucose yield from CSH hydrolysed with 0.5 M H_2SO_4 at 130^oC – 170^oC using two-fraction models

4. CONCLUSION

From the results obtained, it can be concluded that cowpea seed husk can be hydrolysed to produce glucose using sulphuric acid. The maximum glucose yield was obtained at the conditions: 0.5 M acid concentration, 0.02 g/ml substrate concentration, 150ºC, and at 50 minutes reaction time. Acid concentration of 0.5 M gave a better yield than 0.1 M acid concentration which shows that increase in acid concentration increases the yield of glucose. Based on the conditions of this study, Increase in substrate concentrations beyond 0.02 g/ml will reduce the yield of glucose. The experimental data obtained was observed to be suitably described by the two fraction model. The value of the reaction rate constants obtained with 0.5 M acid concentration for sugar formation is higher than the degradation reaction. This justifies the conclusions that increase in acid concentration increases the net yield of glucose. Also, from the results obtained, cowpea seed husk is a good substrate for glucose production.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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