



## Original Research Article

### Development and Test Performance of a Predictive Reaction Model for Moderate Temperature Delignification of Sugarcane Bagasse using Sodium Hydroxide

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#### ABSTRACT

*Reduction of carbon dioxide emission into the atmosphere in order to curb global warming, necessitates harnessing energy from sources other than fossil fuel. Such sources include sugarcane bagasse, whose processing into energy precursor must be preceded by the removal of its protective and recalcitrant lignin layer. This paper developed and simulated a predictive reaction model for low temperature lignin removal from sugarcane bagasse using sodium hydroxide. Results showed increase in degree of delignification with pH up to 10. There was however no significant increase in degree of delignification between pH 10 and 11 for the temperature values studied. Treatments using 0.3 mm particle diameter showed increase de-lignification compared with those for 0.6 and 1.2 mm. A maximum degree of de-lignification of 62.2% was achieved at 50 °C, pH 11, 60 kgm<sup>-3</sup> NaOH concentration and 0.3 mm particle diameter after 48 h. Also, both temperature and pH reduced significantly within 24 h when not controlled at set point resulting in lesser amount of lignin removal. Scanning electron microscopy (SEM) images indicated changes in the morphology of bagasse after NaOH treatments. A modified pseudo-first order kinetics with activation energy of 44.04 kJmol<sup>-1</sup> was found to represent degree of delignification of sugarcane bagasse. The simulated results compared favourably with the experimental results in all of the parameters investigated.*

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## 1. INTRODUCTION

Every activity by man uses energy in one form or another. Hence, domestic and industrial activities depend largely on the availability, quality and accessibility of energy. Also, economic, political and social interactions of nations of the world depend largely on their energy availability and usage. (Fischer-Kowalski

and Schaffartzik, 2015). Consequently, man is inundated with the task of producing or harnessing energy for use. Today, energy accessibility and cost is a viable index for socio-economic and political development of most nations of the world (Vasic *et al.*, 2021)

Energy account of the International Energy Outlook is critical about energy production circle (IEO, 2016). The report suggested a rise in the estimate of impending energy demand all over the world. The report also specified that the global energy need will increase to 815 quadrillion BTU in 2040, an increase of 48% over the figures of 2016. The fundamental energy source today, is the fossil-based fuels because of their advantages which include, high energy intensity, relatively low cost, availability in large amounts and convenience in terms of use and storage (Ballesteros *et al.*, 2006; Uihlein *et al.*, 2009). Arising from the projections of 80% of the entire power generation in 2040 attributable to generation from fossil fuels, it is evident that global greenhouse gas (GHG) emission will increase even further (IEO, 2016). With this scenario, it becomes imperative that the challenge facing the world today is the global reduction in carbon dioxide (CO<sub>2</sub>) emissions by up to 80% because CO<sub>2</sub> is the primary gas that causes global warming (Hadjipaschalis *et al.*, 2009). The consequence of the failure of this is that the universe will become dangerous to all life on earth. The specific and sometimes stringent government and regulatory agencies guidelines, at several levels, in favour of renewable energy source, can be put down to the goal of reduction of 80% CO<sub>2</sub> emission thereby reducing the dangers of life on earth (Akerede *et al.*, 2010).

Ethanol is continuously being given serious attention worldwide not only because of its worth as an energy source substitute to non-renewable gasoline, but also due to the increase price of oil as well as climatic changes with its attendant consequences (Owusu and Asumadu-Sarkodie, 2016). It is also a renewable and viable energy source, efficient and benign to the environment. As a hygienic and flammable energy source, ethanol is considered as a good alternative to replace oil (Thomas and Kwong, 2001).

As a result of the key value of human foodstuff and animal feed, conventional crops used for bioethanol production such as wheat, corn, molasses and sugarcane juice are not available to meet this worldwide demand of bioethanol production. Lignocellulosic biomass, which are abundant, are an inexpensive resource and do not compete with crops as human food and animal feed are now being investigated as viable substitute for food crops. Considerable studies on ethanol production from several lignocellulosic resources have been reported (Akpan, *et al.*, 2005; Gamez *et al.*, 2006; Dawson and Boopathy, 2008; Hendriks and Zeeman, 2009).

Production of bioethanol from lignocellulosic biomass entails essentially four steps with the pretreatment step imposing the greatest challenge because it has to deal with many factors that limit hydrolysis, such as accessibility to the fibres, cellulose crystallinity, and lignin and hemicellulose barrier (Ko *et al.*, 2012). Pretreatment process involves delignification of the feedstock in order to destroy the lignin shell protecting cellulose and hemicelluloses, increase porosity, decrease crystallinity of cellulose to access sugar substrate.

Sugarcane bagasse is a typical example of renewable lignocelluloses biomass. It is a waste cellulose fibre residue derived from sugarcane processing after juice extraction. Sometimes it is disposed through burning. However the increasing cost of fuel oil, natural gas and electricity generation has led renewed interest in bagasse as fuel in a number of sugar mills for electricity generation (Shrestha *et al.*, 2020). The process of sugarcane processing is known to generate large quantity of these wastes which can be used to produce bioethanol and other equally useful products. Delignification of bagasse is conceived to be an intricate process, involving transfer of masses from de-lignifying agent into the raw materials and non-homogeneous chemical reactions between different material constituents employed (Tu *et al.*, 2008). Studies including the works of Baba *et al.*, (2016) and Zhao and Liu, (2013) on kinetics of delignification of lignocellulosic materials have been reported.

Kinetic modelling of a typical Nigerian sugarcane bagasse is not sufficiently documented in spite of its potential for ethanol production as reported by Iye and Bilsborrow (2013). Thus, the findings in this research work will be a good effort in this direction. Also, a global rate equation that simultaneously accounts for conceivable factors that affect rate of lignin removal such as bagasse particle size, concentration of de-

lignifying agent, pH and temperature of contact and time of exposure to de-lignifying agent has not been reported.

## 2. MATERIALS AND METHODS

### 2.1. Bagasse Generation

The schematic diagram of the process used to generate different sizes of sugarcane bagasse is shown in Figure 1.

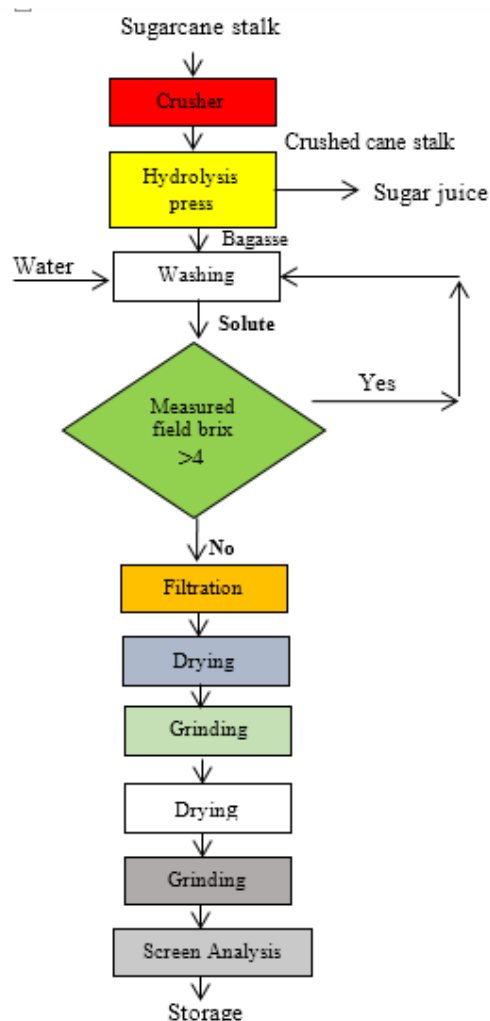


Figure 1: Process flow diagram for bagasse generation

Sugarcane stalks used to produce bagasse for this study was provided by the sugarcane program of National Cereals Research Institute (NCRI) Badeggi, Nigeria. Sugarcane stalks were crushed using a GEFCO heavy duty crusher to obtain sugarcane bagasse. Sugarcane juice was then extracted from bagasse using a hydraulic press resulting in “juice free” bagasse. The bagasse was subsequently washed repeatedly with water until free of sugar juice by measuring the field brix using an Abbey refractometer. This was to ensure that all ethanol subsequently produced was from de-lignified sugarcane bagasse and not from any juice carried over with bagasse. Bagasse solution in water was filtered and the cake dried at room temperature. This was

subsequently ground using a 1.5 kW ASIKO A11 double grinding mill. Screen analysis was then carried out to separate the ground bagasse into various mesh sizes using an automatic sieve shaker D403 by shaking for 30 minutes. The bagasse of each mesh size was stored in mini plastic buckets covered with cotton wool and aluminium foil before placing the lid to avoid absorption of moisture until needed for use.

## 2.2. Delignification at Various Conditions

Sodium hydroxide delignification of 0.3 mm particle diameter sugarcane bagasse was carried out using 3% v/v NaOH solution, with sugarcane bagasse to NaOH concentration of 3% w/v in a 1 litre working volume laboratory fermenter with automatic pH and temperature controls shown in plate 1.



Plate 1: Laboratory reactors with automatic pH and temperature controls

The fermenter temperature was set at 30 °C and controlled at this temperature using an automatic temperature controller attached to the fermenter. Water whose temperature was at least 5 °C lower than the set point temperature was made to circulate from a reservoir through cooling coil attached to the fermenter in order to bring the temperature of the fermenter content to set point as may be necessary. The water used in cooling the fermenter passes through the exit to the drain. A heater, also attached to the fermenter, heats up the fermenter content in order to increase the temperature of the fermenter content as may be necessary to maintain set point temperature. The pH was set and controlled at 8. Control of pH values at set point, was achieved via automatically controlled peristaltic pumps attached to the fermenter that ensured the dosage of appropriate amount of sulphuric acid or sodium hydroxide into the fermenter from separate beaker reservoirs containing these chemicals in order to maintain the pH at set point. Once the pH was above the set point value, a sensor triggers the peristaltic pump to dose in a drop or two of Sulphuric acid to lower the pH and bring it to set point. Similarly, if the pH becomes lower than set point, a sensor triggers the peristaltic pump to dose in a drop or two of NaOH to bring the pH to set point. Care was taken to ensure that the dosage of acid or base did not compromise the concentration of de-lignifying agent or solid loading being studied. In all the study, temperature was controlled at set point  $\pm 1$  °C while the pH was controlled at set point  $\pm 0.2$ . By successively changing the temperature values to 40 and 50 °C, pH values successively to 9, 10 and 11 and successively changing bagasse particle size from 0.3 mm to 0.6 and 1.2 mm other treatment conditions were similarly treated.

## 2.3. Preparation of Lignin Concentration Calibration Curve

Standard lignin samples, obtained from Federal University of Technology, Minna, Nigeria was used to prepare the calibration chart for subsequent lignin measurements. Known concentrations of lignin, obtained by dissolving known masses of sample lignin in hydrogen peroxide were prepared and their absorbance measured at 320 nm. The graph of lignin concentrations against absorbance values was obtained and subsequently used for lignin concentration measurements.

## 2.4. Measurement of Lignin Concentration and Calculation of Degree of Delignification

De-lignification was monitored every 6 h by measuring the absorbance of samples taken at 320 nm. The absorbance was measured two times and the average reading recorded. For sampling, a syringe was used to withdraw about 20 ml of the fermenter content by creating a vacuum within the sample bottle. The sample taken was filtered through Whatman filter paper and the absorbance of the filtrate was measured at 320 nm. After 48 h, the fermenter content was emptied into a beaker and then filtered through Whatman filter paper and the residue washed with distilled water. The calibration curve was used to obtain the corresponding lignin concentration. Degree of delignification was subsequently calculated using Equation 1.

$$D = \frac{C_{L0} - C_{i(t)}}{C_{L0}} \times 100 \quad (1)$$

Where  $D$ =degree of delignification,  $C_{L0}$ = initial lignin concentration ( $gm^{-3}$ ),  $C_{i(t)}$ = lignin concentration at any time ( $gm^{-3}$ )

## 2.5. Development of Predictive Reaction Model

Concentration of reactants, temperature, time, pH values, mass transfer characteristics all affect the rate of reaction (Levenspiel, 2004). Delignification of sugarcane bagasse is considered to be a chemical reaction process where some or all of these factors play out. Delignification of sugarcane bagasse is conceived to be a process, involving mass transfer of de-lignifying solvent into the raw material and heterogeneous chemical reaction between different material components and the chemicals (Tu *et al.*, 2008; Wang *et al.*, 2011; Baba *et al.*, 2016). In earlier kinetic studies on sugarcane bagasse delignification, Zhao and Liu (2013), reported kinetics of delignification to be well represent by a modified pseudo- first order kinetics in terms of degree of delignification ( $D$ ) defined by Equation 2.

$$\frac{dD}{dt} = K_1(1 - D) \quad (2)$$

The degree of delignification is defined in terms of lignin concentration by Equation 1.

$K_1$  = Rate constant ( $s^{-1}$ ).

Hence at time zero, the degree of delignification is zero. Equation (2) depicts that the degree of delignification follows a first order reaction kinetics with respect to unreacted lignin fraction. The equation also suggests that typically, given the right conditions, 100% degree of delignification is attainable indicating that all the lignin content is theoretically recoverable from sugarcane bagasse.

Integrating Equation 2 yields Equation 3.

$$\ln(1 - D) = K_1 t \quad (3)$$

Equation (3) suggests that a plot of  $\ln(1 - D)$  against the reaction time  $t$  should give a straight line passing through the origin. However, many researchers in earlier works have shown that this is not the case and a straight line passing through the origin is not obtained with the plotting of Equation 3. (Wang *et al.*, 2011; Zhao and Liu, 2013; Baba *et al.*, 2016). This discrepancy shows that the kinetic model suggested by equation (3) if not modified cannot describe accurately the kinetics of lignin removal from Sugarcane Bagasse. Consequently, a novel kinetic model was proposed by Zhao and Liu (2013) to more accurately represent the kinetic of delignification of sugarcane bagasse by introducing a term which is representative of lignin that cannot be removed no matter the level of severity imposed. Hence Equation 2 was modified to obtain Equation 4 with the introduction of a limiting term called potential degree of delignification ( $d_D$ ).

$$\frac{dD}{dt} = K_1(d_D - D) \quad (4)$$

Integrating Equation 4 yields Equation 5.

$$\int_0^D \frac{dD}{d_D - D} = K_1 \int_0^t dt$$

$$D = d_D [1 - \exp(-K_1 t)] \quad (5)$$

### 2.5.1. Effects of temperature and pH on delignification

The constant  $K_1$  in Equation 5 is a function of temperature, hence,

$$K_1 = f(T) \quad (6)$$

The dependency of  $K_1$  on temperature may be expressed by the Arrhenius equation of the form:

$$K_1 = K_0 \exp\left(-\frac{E}{RT}\right) \quad (7)$$

Where  $K_0$ = Arrhenius constant,  $E$ =activation energy,  $R$ = universal gas constant,  $T$ = absolute temperature.

Putting Equation 7 into Equation 5 yields Equation 8.

$$D = d_D \left[ 1 - \exp\left\{-K_0 \exp\left(\frac{-E}{RT}\right)\right\} t \right] \quad (8)$$

Dawson and Boopathy (2008) reported the linear dependency of delignification with respect to  $H_2O_2$  concentration. Finally, on incorporation of pH effects into the rate equation, Equations 8 and 9 was proposed to represent the global rate equation for sodium hydroxide delignification where there are no pore diffusion resistances.

$$D = d_D \left[ 1 - \exp\left\{-K_0 \exp\left(\frac{-E}{RT}\right) C_{NaOH} pH^\beta t\right\} \right] \quad (9)$$

Zhao and Liu (2013), have also reported that the potential degree of delignification correlated well with the experimental severity conditions imposed (temperature and catalyst concentration). Correlating the potential degree of delignification with the severity conditions (temperature, concentration of delignifying agent and pH) using similar form of equation as Zhao and Liu (2013) Equation 10 is proposed.

$$d_D = 1 - \frac{A}{C_{NaOH} T^m pH^n} \quad (10)$$

Where  $A$ ,  $m$  and  $n$  are constants to be determined.

Putting Equation 10 into Equation 9 yields Equation 11.

$$D = \left( 1 - \frac{A}{C_{NaOH} T^m pH^n} \right) \left[ 1 - \exp\left\{-K_0 \exp\left(\frac{-E}{RT}\right) C_{NaOH} pH^\beta t\right\} \right] \quad (11)$$

Equation (11) can be written in a more concise form given in Equation 12.

$$D = d_D [1 - \exp(-K_{obs}t)] \quad (12)$$

Where  $d_D$  is given by Equation 10 and  $K_{obs}$  by Equation 13.

$$K_{obs} = K_0 \exp\left(\frac{-E}{RT}\right) C_{NaOH} pH^\beta \quad (13)$$

Baba *et al.* (2018) developed an equation for the pore diffusion resistance given by Equation 14.

$$\eta = \frac{\tanh\phi_1 L}{\phi_1 L} \quad (14)$$

where  $\eta$  = effectiveness factor,  $\phi_1$  = Thiele modulus and  $L$  = particle diameter

On substituting in Equation 11, the reaction rate model becomes:

$$D = \frac{\tanh\phi_1 L}{\phi_1 L} \left\{ \left( 1 - \frac{A}{C_{NaOH} T^m pH^n} \right) \left[ 1 - \exp\left\{ -K_0 \exp\left(\frac{-E}{RT}\right) C_{NaOH} pH^\beta t \right\} \right] \right\} \quad (15)$$

## 2.6. Analytical Method

Composition of bagasse was determined prior to de-lignification as described by Krishna and Ranhan (1980) to ascertain the lignin, cellulose, hemicellulose and ash content Masses used in this work were taken using AL 204 Mettler Toledo balance while pH measurements were taken using HI 2211 pH/ORP meter. The sugar content in the liquid extract from sugarcane bagasse was determined using Abbey refractometer. Absorbance of the extract were taken using JENWAY 6705 UV/Vis spectrophotometer.

## 2.7. Mathematical Model Simulation

MathCAD version 14.0 (2007) was used to simulate the mathematical model developed in this study. MathCAD is a highly efficient computer software developed by Parametric Technology Corporation (PTC) for the verification, validation, documentation and use by professional engineers and scientists. It allows calculations, graphical analysis, programming and simulations to be carried out in such a user friendly environment that it has become a ubiquitous tool for today's engineers and scientists. The software ware was used to minimize the objective function ( $f$ ) which was the quadratic sum of the difference between the experimental data  $y_i$  and the simulated data  $f(x_i)$  given by Equation 16.

$$f = \sum_{i=1}^{i=n} [y_i - f(x_i)]^2 \quad (16)$$

## 3. RESULTS AND DISCUSSION

### 3.1. Composition of Sugarcane Bagasse

Table 1 shows the composition of sugarcane bagasse. Table 1 indicates that cellulose and hemicelluloses combined, accounted for over 74% of bagasse, which can be treated to obtain fermentable sugars. This percentage is a motivating factor for further removal of lignin to expose the cellulose and hemicellulose to further treatments to fermentable sugars.

Composition	% by weight
Lignin	22.0
Cellulose	43.2
Hemicellulose	31.5
Ash	3.3

### 3.2. Calibration Chart for Measurement of Lignin Concentration

The calibration chart, obtained by the use of UV spectroscopy at wavelength of 320 nm, used to estimate lignin concentration is shown in Figure 2. This wave length was selected because at 320 nm wave length, interference due to other compounds such as furfural is negligible (Wang *et al.*, 1999). The calibration curve shows a linear relationship between lignin concentration and absorbance at 320 nm. This is similar to the calibration curve obtained by previous researchers (Wang *et al.*, 1999 and Zhao and Liu, 2013).

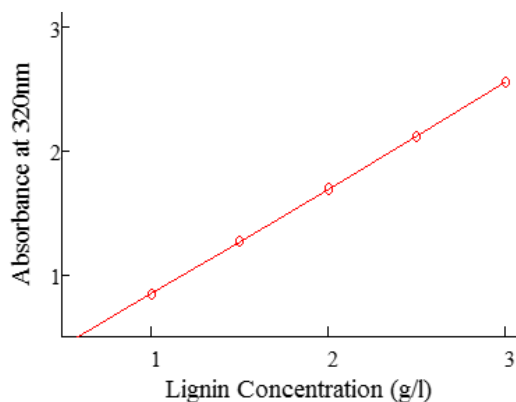


Figure 2: Calibration chart for lignin concentration

### 3.3. Variation of Uncontrolled pH and Temperature with Time

Time variation of uncontrolled pH values during lignin removal from sugarcane bagasse using NaOH is presented in Figure 3.

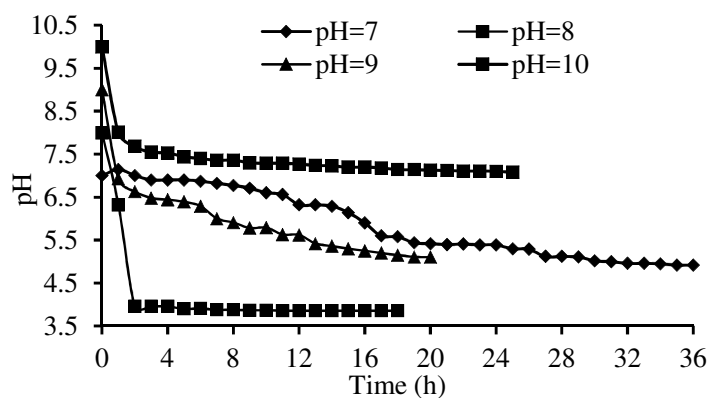


Figure 3: Variation of uncontrolled pH with time



The results showed a significant reduction in pH values within few hours when pH was not controlled for all initial pH values studied. For example, pH values reduced from initial values of 10 and 9 to 7 and 6 respectively within a period of 7 h. This may be put down to secretion of acidic substances in the course of delignification process. Hence the need to control pH values at set point in order to have accurate knowledge of pH effects on delignification of sugarcane bagasse. Although data is not presented here for temperature variations, it is well understood that uncontrolled set point temperature will reduce in temperature as delignification progresses as a result of heat losses by conduction and convection (Wang *et al.*, 2021).

### 3.4. Experimental Delignification using 3% NaOH and 0.3 mm Diameter Sugarcane Bagasse

Results of sugarcane bagasse degree of delignification using 3% NaOH on 0.3 mm particle diameter sugarcane bagasse presented in Table 2 for pH 8-11 and temperature 30, 40 and 50 °C showed that in general, lignin removal increased with reaction time (0 - 48 h), temperature (30, 40 and 50 °C) and pH values (8, 9, 10 and 11). For instance, at pH 8 and 30 °C, Table 2 shows that between 0 and 48 h, delignification increased from 0 to 14.92%. The corresponding percentage increase for 40 and 50 °C treatments at the same pH value of 8 were 25.36 and 23.09%. Table 2 also showed that on increasing the pH from 8 to 11, the percentage degree of delignification after 48 h increased from 14.92 to 39.92% for the same temperature of 30 °C. The corresponding values for 40 and 50 °C treatments were from 25.36 to 44.39% and from 23.09 to 50.49% respectively. Generally therefore, delignification increases with increase in temperature for each of the pH values 8, 9, 10 and 11. For any selected temperature value, the effect of pH variation on delignification characteristics is shown by the comparison of corresponding rows of the temperature value selected. For example, increasing pH value from 8 through 10 to 11 and temperatures values from 30 through 40 to 50 °C, the degree of delignification increased from 14.92 through 25.36 to 23.09% for pH 8 to 35.92% through 38.39 to 50.39% for pH 10 to 39.92% through 44.39 to 50.49% for pH 11 respectively. Therefore as pH increases from 8 to 11, degree of delignification increase for all temperatures 30, 40 and 50 °C. However, increase delignification between pH 10 and 11 appears not to be significant compared to increase in delignification consequent upon increase in pH from 8 to 9 or from 9 to 10. Lignin removal was observed to progress faster within the first 24 h and then more slowly in the next 24 h. This trend is consistent with the result reported by Baba *et al.* (2016). The later sluggishness in delignification may be attributable to the secretion of inhibitory products such as furfural and also due to condensation reactions (Wang *et al.*, 1999). Notwithstanding, this reaction is not significant compared with lignin removal reaction.

Table 2: Effect of time, temperature and pH on delignification of 0.3 mm diameter bagasse using 3% NaOH

pH	8	9	10	11	8	9	10	11	8	9	10	11
Temperature (°C)	30				40				50			
Time (h)	Degree of delignification (%)											
6	10.84	3.12	8.84	10.84	14.84	14.84	14.94	15.84	14.84	14.84	21.84	20.84
12	11.86	11.86	17.86	19.86	16.81	16.81	23.81	20.81	16.81	18.81	33.81	40.93
18	11.91	20.41	19.91	23.91	18.21	21.11	28.11	26.11	19.11	22.11	39.11	42.64
24	11.79	22.89	21.79	26.79	19.19	26.09	30.09	33.09	22.09	25.09	42.09	43.91
30	13.45	29.91	22.45	33.45	20.25	29.35	31.35	36.35	22.35	32.35	46.35	46.53
36	14.65	30.30	33.65	36.65	21.49	33.35	32.35	38.35	22.95	34.35	47.35	48.31
42	14.11	32.19	34.11	38.11	22.86	39.21	34.21	41.21	23.01	35.21	49.21	49.72
48	14.92	33.32	35.92	39.92	25.36	39.99	38.39	44.39	23.09	35.39	50.39	50.49

### 3.5. Experimental Delignification using 6% NaOH and 0.3 mm Diameter Sugarcane Bagasse

Concentration of de-lignifying agent is one of the factors conceived to affect the amount of lignin that can be removed from lignocellulosic material such as sugarcane bagasse (Zhao and Liu, 2013; Rojith and Singh, 2013). To study the effects of initial concentration of the de-lignifying agent, concentration of NaOH was doubled to 6% from 3%. The general trends observed was similar to those observed for treatment using 3% NaOH. For example, for pH values 8,9,10 and 11 and temperature 30, 40 and 50 °C, Table 3 indicated initial

step increase in lignin removal with time followed by a gradual increase in lignin removal after about 24 h. The later reduction in delignification rate may be as result of secretion of inhibitory substances such as furfural (Wang et al., 2013). Comparison of Table 3 for delignification using 6% NaOH at pH values of 8, 9, 10 and 11 respectively with Table 2 for delignification using 3% w/v concentration of NaOH also at the same pH values showed an increase in delignification values for all temperatures and pH values studied. However, when the concentration of the de-lignifying agent was doubled, the increase in delignification consequent upon this 100% increase in concentration were far less than 100%. For instance, comparison of degree of delignification values using 3 and 6% concentrations of NaOH for selected times of 12, 24, 36 and 48 h and pH 11 and 30 °C, increased by only 26, 14.6, 17.1 and 26.8% respectively. This suggests that increasing concentration values beyond 3% may not be economical especially where sugarcane bagasse is sufficiently available. Similar trends were observed for all pH and temperature values. This finding is in agreement with the findings reported by Zhao and Liu (2013). he reduced delignification at higher concentrations of 6% may be as a result of the rapid evolution of oxygen consequently reducing the oxygen incorporation at lignin sites with the consequent result of reduction in delignification efficiency.

Table 3: Effect of time, temperature and pH on delignification of 0.3 mm diameter bagasse using 6% NaOH

pH	8	9	10	11	8	9	10	11	8	9	10	11
Temperature (°C)	30				40				50			
Time (h)	Degree of delignification (%)											
6	10.84	01.84	14.84	17.02	18.40	10.84	14.84	23.23	19.01	14.84	26.45	26.25
12	16.86	16.86	25.89	27.21	18.81	18.81	26.81	32.03	21.21	18.81	38.91	30.21
18	19.91	18.91	33.91	33.12	21.11	22.11	31.11	39.23	23.12	22.11	46.51	46.56
24	22.79	24.79	36.79	37.77	22.09	28.09	36.09	45.02	24.21	27.09	51.20	50.03
30	22.45	28.45	42.45	42.01	24.35	32.35	42.35	49.16	24.78	31.35	54.21	52.32
36	26.65	31.65	47.65	49.03	25.35	37.35	46.35	52.02	25.01	33.35	56.32	54.21
42	26.61	32.11	49.11	51.02	26.21	38.21	49.21	54.13	25.21	34.21	57.87	59.56
48	26.92	33.92	49.92	53.06	27.39	39.39	54.39	56.02	26.39	34.99	59.91	62.21

### 3.6. Experimental Delignification using 3% NaOH and 0.6 and 1.2 mm Diameter Sugarcane Bagasse

In order to study the effects of particle diameter on delignification characteristics, particle size was doubled from 0.3 mm to 0.6 and 1.2 mm diameter and the results are shown in Tables 4 and 5.

Table 4: Effect of time, temperature and pH on delignification of 0.6 mm diameter bagasse using 3% NaOH

pH	8	9	10	11	8	9	10	11	8	9	10	11
Temperature (°C)	30				40				50			
Time (h)	Degree of delignification (%)											
6	5.84	8.84	11.84	08.85	14.84	14.84	13.84	11.84	14.84	15.84	23.84	23.56
12	8.86	11.86	18.86	16.86	16.81	16.81	20.86	21.81	16.81	17.81	33.86	26.00
18	9.91	18.91	24.91	20.71	17.11	21.11	26.91	24.11	18.11	23.11	37.91	29.00
24	11.79	20.79	26.79	20.79	19.09	22.09	28.79	26.09	19.09	24.09	39.79	36.01
30	11.45	26.45	27.45	28.45	20.35	22.35	30.45	28.35	20.35	24.35	41.45	37.02
36	12.65	27.65	28.65	29.40	21.35	23.35	31.65	30.35	21.35	25.35	43.65	38.71
42	13.11	27.11	30.11	31.41	22.21	26.21	33.11	31.21	22.24	27.21	44.11	39.39
48	13.92	28.02	32.92	33.20	22.36	27.99	34.92	32.39	24.39	29.39	45.92	40.01

The general trend of percentage increase in delignification with time (0-48 h), temperature (30-50 °C), pH (8-11) presented earlier in Table 2 for treatment of 0.3 mm particle diameter sugarcane bagasse was observed also for treatment of 0.6 and 1.2 mm treatment but to lesser percentages. For example, comparison of 0.3 mm particle diameter treatment with 0.6 mm particle diameter treatment, all other factors remaining the same, showed that while the increase in percentage delignification for pH 8 treatment at 30, 40 and 50 °C were 14.92, 25.36 and 23.09% for 0.3 mm particle the values were 13.92, 22.39 and 24.39% respectively for 0.6 mm diameter particles. These lesser percentage increase can be attributed to pore diffusion resistances.

Furthermore, comparison of these two particle sizes at pH 9 showed that while the increase in percentage delignification for pH 9 treatment at 30, 40 and 50 °C were 33.32, 39.99 and 35.39% for 0.3 mm particle the values were 28.02, 27.39 and 29.39% respectively for 0.6 mm diameter particles. Similar trends were observed for 1.2 mm particle diameter as shown in Table 5.

Table 5: Effect of time, temperature and pH on delignification of 1.2 mm diameter bagasse using 3% NaOH

pH	8	9	10	11	8	9	10	11	8	9	10	11
Temperature (°C)	30				40				50			
Time (h)	Degree of delignification (%)											
6	6.02	5.84	11.84	11.81	6.84	10.84	19.84	17.84	6.84	6.84	16.84	23.84
12	7.73	10.86	16.86	16.87	14.84	14.81	20.86	19.81	13.81	10.81	23.81	25.81
18	14.99	15.91	20.91	20.91	15.11	16.11	23.91	23.11	14.11	13.11	28.11	27.71
24	16.89	18.79	21.79	23.79	16.09	20.09	24.09	24.11	15.09	16.09	31.09	29.09
30	17.91	20.45	22.45	25.45	17.35	22.35	25.45	25.35	16.33	17.35	33.35	31.35
36	18.89	21.65	23.65	26.65	18.35	23.35	26.05	26.35	17.21	21.35	34.35	35.35
42	20.01	22.11	24.11	27.11	18.81	24.21	27.01	27.21	18.21	22.21	35.21	37.21
48	20.98	23.92	25.92	28.92	19.39	25.39	27.41	28.39	19.41	24.39	36.39	38.39

### 3.7. Comparative Experimental and Simulated Global Reaction Rate for Delignification using 3% NaOH and 0.3 mm Sugarcane Bagasse

The regressed kinetic constants obtained using Levenberg-Marquardt optimization procedure of MatCad is presented in Table 6 for optimum conditions of pH values of 10 and 11 using 0.3 mm diameter bagasse with NaOH treatment. The activation energy determined was 63.44 kJ/mol which was in agreement with value obtained by Zhao and Liu (2013). Average values of pre-exponential factors shown in Table 6 were used in Equation 15 to obtain the simulated global reaction rate Equation 17.

$$D = \left( 1 - \frac{33.471}{C_{NaOH} T^{1.099} (pH)^{0.51}} \right) \left[ 1 - \exp \left\{ -2.587 \exp \left( \frac{-6.344 \times 10^4}{RT} \right) C_{NaOH} (pH)^{10.27} t \right\} \right] \quad (17)$$

Comparison of experimental and simulated degree of delignification using Equation 17 results for 0.3 mm particle diameter treated with 3% de-lignifying agents as a function of treatment time as shown in Figures 4 and 5 for pH 10 and 11 respectively. These figures indicated that the model could satisfactorily predict the experimental results.

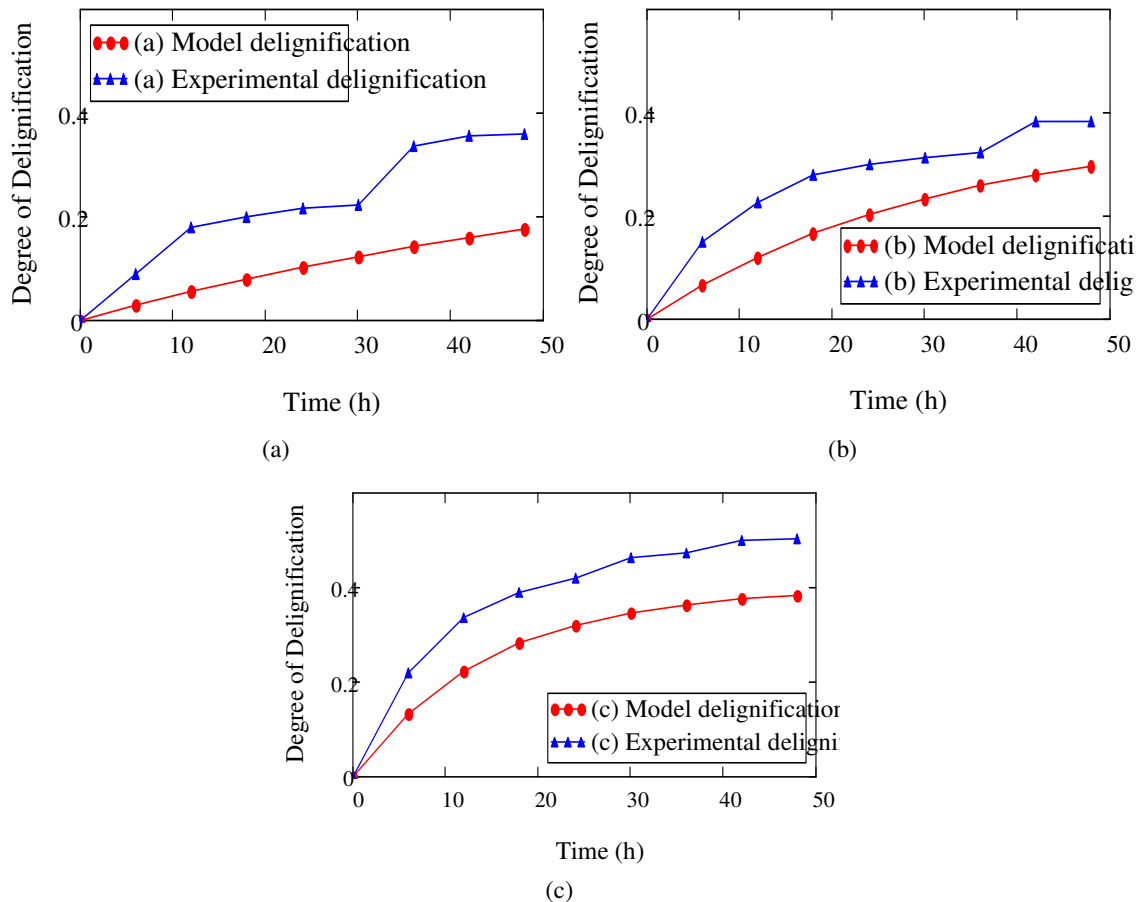
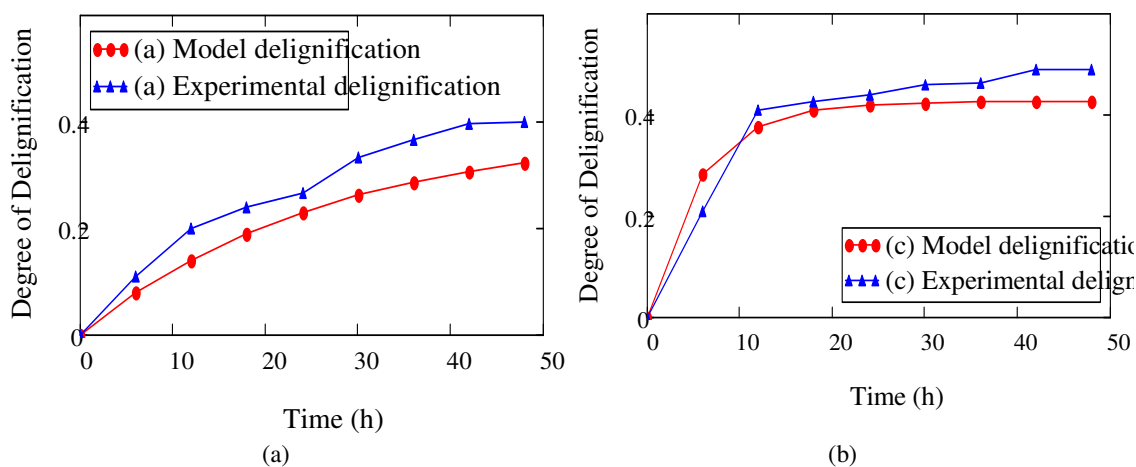


Figure 4: Comparison of experimental and simulated model degree of delignification of 0.3 mm bagasse at pH 10 (a) 30 °C, (b) 40 °C, (c) 50 °C



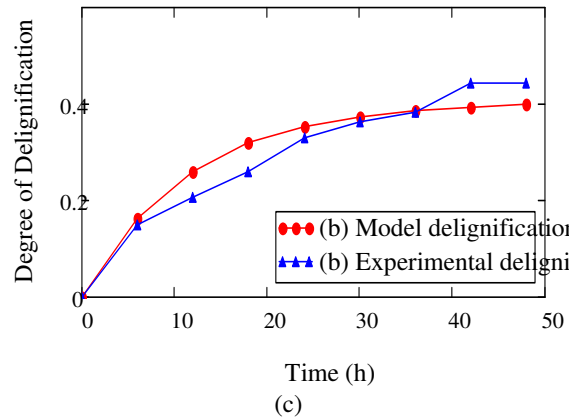


Figure 5: Comparison of experimental and simulated model degree of delignification of 0.3 mm bagasse at pH 11 (a) 30 °C, (b) 40 °C, (c) 50 °C

### 3.8. Comparative Experimental and Simulated Global Reaction rate for Delignification using 3% NaOH and 0.6 or 1.2 mm Sugarcane Bagasse

Average values of pre-exponential factors shown in Table 6 were used in Equation 15 to obtain the simulated global reaction rate Equation 18.

$$D = \frac{\tanh(600D_p)}{600D_p} \left( 1 - \frac{33.471}{C_{NaOH} T^{1.099} (pH)^{0.51}} \right) \left[ 1 - \exp \left\{ -2.587 \exp \left( \frac{-6.344 \times 10^4}{RT} \right) C_{NaOH} (pH)^{10.27} t \right\} \right] \quad (18)$$

Comparison of experimental and simulated degree of delignification using Equation 18, results for 0.6 and 1.2 mm particle diameter treated with 3% de-lignifying agents as a function of treatment time as shown in Figures 6 and 7 for pH 10 and 11 respectively. These figures indicated that the model could satisfactorily predict the experimental results.

Table 6: Kinetic parameters

Kinetic constants	pH				Average Values
	8	9	10	11	
K	0.4	4.089×10 <sup>-4</sup>	3.283	1.891	2.587
β	7.178	6.506	10.54	9.874	10.207
E	1.608 × 10 <sup>4</sup>	1.526 × 10 <sup>4</sup>	6.514 × 10 <sup>4</sup>	6.174 × 10 <sup>4</sup>	6.344 × 10 <sup>4</sup>
A	217.504	0.289	21.748	45.194	33.471
m	1.75	-0.307	1.055	1.144	1.099
n	0.45	2.072	0.47	0.55	0.51

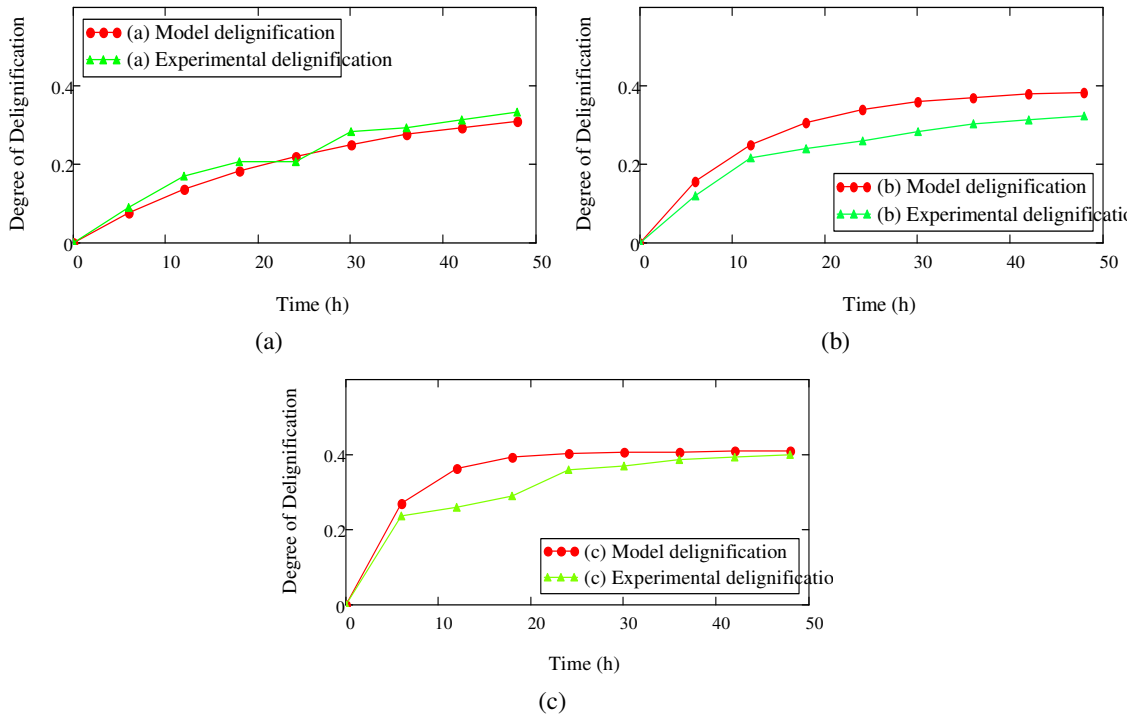
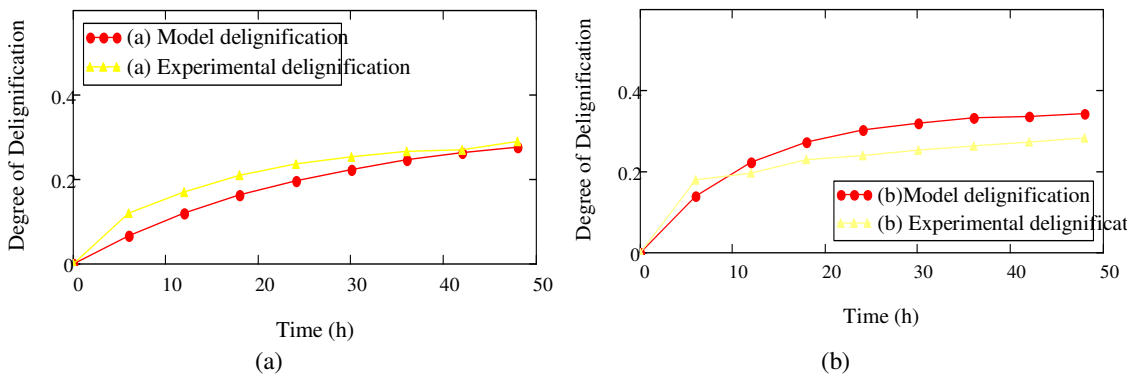


Figure 6: Comparison of experimental and simulated model degree of delignification of 0.6 mm bagasse at pH 10 (a) 30 °C, (b) 40 °C, (c) 50 °C



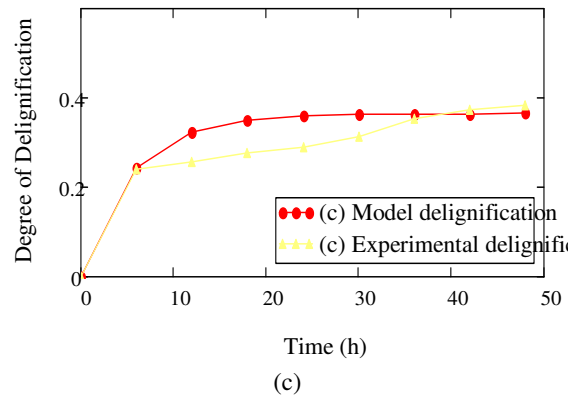


Figure 7: Comparison of experimental and simulated model degree of delignification of 0.6 mm bagasse at pH 11 (a) 30 °C, (b) 40 °C, (c) 50 °C

### 3.9. Morphological Structure of Sugarcane Bagasse

The scanning electron microscopy (SEM) images of sugarcane bagasse before and after delignification at optimum conditions of treatments using 3% NaOH at 50 °C and pH 11 is presented in plates 2 and plate 3 respectively. The SEM micrographs show that the crystal structure is similar with the one after treatment with NaOH showing larger pores indicating lignin solubilisation consequent upon treatment with the delignifying agents (Long *et al.* 2013). The SEM micrograph of untreated bagasse was observed to be smooth and plump with the lignin working as the binding and supporting medium. After lignin solubilisation sequel to the treatments, the morphology of the material was significantly altered and the complete framework of the raw bagasse was destroyed resulting in a rough but conglomerate texture in which the cellulose fibre bundles and some pores of variant sizes were visible.

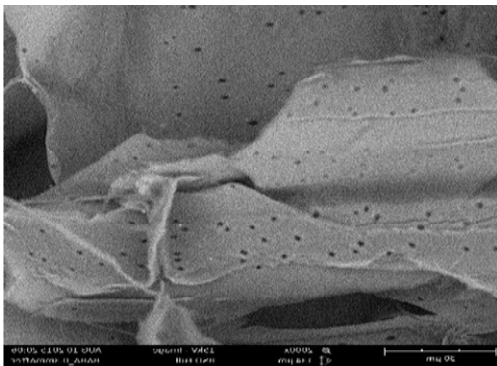


Plate 2: Scanning electron microscopy image of sugarcane bagasse before delignification

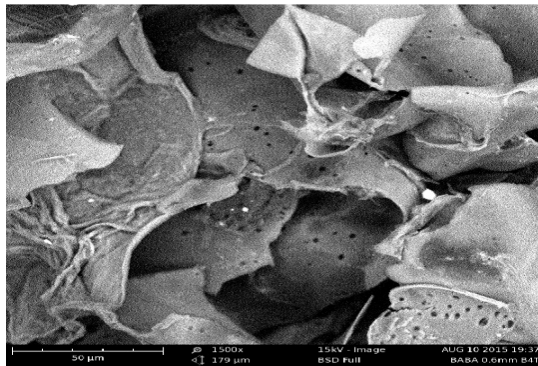


Plate 3: Scanning electron microscopy image of sugarcane bagasse after delignification

## 4. CONCLUSION

In this study it was concluded that uncontrolled pH values during de-lignification of sugarcane bagasse using sodium hydroxide causes a sharp reduction in pH from set point within few hours. Also, de-lignification of sugarcane bagasse using sodium hydroxide gives maximum lignin removal after 48 hours at controlled pH of 11 and temperature of 50 °C using 0.3 mm particle diameter and 3% NaOH concentration. There was no

appreciable increase in lignin removal beyond pH of 11 and for particle size less than 0.3 mm for temperatures values studied.

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## 6. CONFLICT OF INTEREST

There is no conflict of interest associated with this work.

## REFERENCES

- Akerede, H., Hizam, H. and Pouresmaeil, E. (2010). Distributed energy resources and benefits to the environment. *Renewable and Sustainable Energy Reviews*, 14(2), pp. 724-734.
- Akpan, U. G., Kovo, A. S., Abdullahi, M. and Ijah, J. J. (2005). The Production of Ethanol from Maize cobs and Groundnut Shells. *AU Journal of Technology*, 9(2), pp. 106-110.
- Baba, A. H., Aberuagba, F., Onifade, K. R. and Ishaq, M. N. (2016). Kinetic modelling and De-lignification Characteristics of Nigerian Sugarcane Bagasse Using Hydrogen Peroxide. *Journal of Biobased Materials and Bioenergy*, 10(5), pp. 323-329.
- Ballesteros, I., Negro, M. J., Cabanas, A., Manzanares, P., and Ballesteros, M. (2006). Ethanol production from steam explosion pretreated wheat straw. *Applied Biochemistry and Biotechnology*, 130, pp. 496-508.
- Dawson, L. and Boopathy, R. (2008). Cellulosic Ethanol Production from Sugarcane Bagasse without Enzymatic Saccharification. *Bioresources*, 3(2), pp. 452-460.
- Fischer-Kowalski, M. and Schaffartzikk, A. (2015). Energy availability and energy sources as determinants of societal development in a long-term perspective. *MRS Energy & Sustainability*, 2, p. E1
- Gamez, S., Gonzalez-Cabriales, J. J., Ramirez, J. A., Garrotte, G. and Vazquez, M. (2006). Study of the Hydrolysis of Sugar Cane Bagasse Using Phosphoric Acid. *Journal of Food Engineering*, 74(1), pp. 78-88.
- Hadjipaschalis, I., Kourtis, G. and Poullikkas, A. (2009). Assessment of oxyfuel power generation technologies. *Renewable and Sustainable Energy Reviews*, 13(9), pp. 2637-2644.
- Hendriks, A. T. W. M. and Zeeman, G. (2009). Pretreatments to Enhance Digestibility of Lignocellulosic Biomass. *Bioresource Technology*, 100(1), pp. 10-18.
- International Energy Outlook (IEO). (2016). *International Energy Outlook*. Retrieved from [http://www.eia.gov/forecasts/ieo/pdf/0484\(2016\).pdf](http://www.eia.gov/forecasts/ieo/pdf/0484(2016).pdf)
- Iye, E. L. and Bilsborrow, P. E. (2013). Cellulosic Ethanol Production from Agricultural Residues in Nigeria. *Energy Policy*, pp. 207-214.
- Ko, C. H., Wang, Y. N., Chang, F. C., Chen, J. J., Chen, W. H. and Hwang, W. S. (2012). Potentials of Lignocelluloses Bioethanols Produced from Hardwood in Taiwan. *Energy*, 44(1), pp. 329-334.
- Krishna, G. and Ranhan, S. K. (1980). *Laboratory manual for Nutritional Research*. New Delhi, India. Vikas Publishing House, PVT ltd.
- Levenspiel, O. (2010). *Chemical Reaction Engineering*. New Delhi, India: Wiley India Pvt. Ltd.
- Long, J., Li, X., Guo, B., Wang, L. and Zhang, N. (2013). Catalytic Delignification of Sugarcane Bagasse in the Presence of Acidic ionic Liquids. *Catalysis Today*, 200, pp. 99-105.
- Owusu, P. A. and Asumadu-Sarkodie, S. (2016). A review of renewable energy sources, sustainability issues and climate change mitigation. *Cogent Engineering*, 3(1), p. 1167990.



- Rojith, G. and Singh, I. S. (2013). Hydrogen peroxide pretreatment efficiency comparison and characterization of lignin recovered from coir pith black liquor. *Journal of Environmental Research and Development*, 7(4), pp. 1333-1339
- Shrestha, N., Tripathi, A. K.K., Govil, T., Sani, R. K., Urgun-Demirtas, M., Kasthuri, V and Gadhamshetty, V. (2020). Electricity from Lignocellulosic Substrates by Thermophilic *Geobacillus* species. *Scientific reports*, 10(1), pp. 1-9.
- Thomas V. and Kwong, A. (2001). Ethanol as a lead replacement: Phasing out gasolin in Africa. *Energy Policy*, 29(13), pp. 1133-1143.
- Tu, Q., Fu, S., Zhan, H., Chai, X. and Lucia, L. A. (2008). Kinetic Modelling of Formic acid pulping of Bagasse. *Journal of Agricultural and Food Chemistry*, 56(9), pp. 3097-3101.
- Uihlein, A. and Schebek, L. (2009). Environmental Impacts of a Lignocellulosic feedstock biorefinery System: An assessment. *Biomass and Bioenergy*, 33, pp. 793-802.
- Vasic, K., Knez, Z. and Leigeb, M. (2021). Bioethanol Production by Enzymatic Hydrolysis from Different Lignocellulosic Sources. *Molecules*, 26(3), p. 753.
- Wang, J., Minami, E., Asmadi, M. and Kawamoto, U. (2021). Effect of delignification on the thermal degradation reactivity of hemicellulose and cellulose in wood cell walls. *Journal of wood science*, 67(1), pp. 1-11.
- Wang, K., Yang, H. Chen, Q. and Sun, R. (2013). Influence of delignification efficiency with alkaline peroxide on the digestibility of furfural residues for bioethanol production. *Bioresource Technology*, 146, pp. 208-214.
- Wang, Q., Chen, K., Liu, S., Li, J. and Xu, J. (2011). Kinetics of Bagasse Delignification by Using High Boiling Solvents. *BioResource*, 6(3), pp. 2366-2374.
- Wang, Q. H., Kuninobu, M., Ogawa, H. I. and Kato, Y. (1999). Degradation of volatile fatty acids in highly efficient anaerobic digestion. *Biomass and Bioenergy*, 16, pp. 407-416.
- Zhao, X. and Liu, D. (2013). Kinetic Modeling and mechanisms of Acid-Catalyzed Delignification of Sugarcane Bagasse by Aqueous Acetic Acid. *Bioenergy Research*, 6(2), pp. 436-447.