



# KINETICS STUDY OF HYDROLYSIS REACTION OF SAWDUST OF HARDWOOD, SOFTWOOD AND MIXED SAWDUST USING MILD SULFURIC ACID.

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## Key Words

Hydrolysis of wood, Acidic hydrolysis of Hardwood and Softwood, Kinetics of sawdust hydrolysis, mild sulfuric acid hydrolysis of wood materials.

## ABSTRACT

Biofuel from lignocellulosic biomass is likely going to become the major key sources of renewable energy in the near future in order to combat the impact of global warming and the depletion of fossil fuel resources. During hydrolysis reaction, low sugar recovery is the major bottle neck due to different factors that influence hydrolysis reaction. This research work investigates glucose yield through acidic hydrolysis of Mahogany sawdust, Ako sawdust and mixed sawdust of different wood after Hydrogen Peroxide Acetic Acid (HPAC) pre-treatment. Variation of acid concentrations of 1M, 1.5M, 2M, 2.5M and 3M were studied. The optimal glucose yield of 59mg/ml, 58mg/ml and 55mg/ml were recorded for mixed sawdust, Softwood and Hardwood respectively at 2M. The findings from hydrolysis reaction show that there is a gradual increase in yield of glucose as the concentration of acid increases, this continues till optimal glucose yield, after which there is low sugar recovery due to side reaction producing bye products. The specific reaction rate constant for acid hydrolysis were 0.016, 0.0192 and  $0.0173\text{min}^{-1}$  for Mahogany, Ako and mixed sawdust respectively.

## Introduction

The world's energy needs are mainly reliant on non-renewable fossil fuel which are derivatives of crude oil, almost 90 % of the product are used for generation of energy and mobility among others. The problem of population explosion has led many developed and developing economies to increase their industrial activities, leading to rapid energy demands. It is certain to conclude that, fossil fuels which are the source of coal, natural gas and oil which are non-renewable energy with time will be scare as a result of depletion and inevitably exhausted, and over reliance on them at the expense of the climate for decades has led to a huge climatic change such

as global warming due to emissions of greenhouse gas. Therefore, it is important to explore every possibility of using alternative source of energy, which are renewable, eco-friendly and even more efficient than fossil fuel, thus, bioethanol fermentation is key and integral [1]. Renewable energy such as biofuels is a perfect replacement for fossil fuels and a worth solution to economic challenges confronting the world and to the impact of climate change. Recently, more attention is devoted to biofuels production and its uses as the alternative which will help to reduce greenhouse gas emissions. The drastic rise in demand for ethanol use as a raw material for production of other chemicals and as a fuel for Automobiles, economic and domestic activities like energy source, preservatives, solvents for industrial processes, cleansing agents, and its unique role in fighting greenhouse gas emissions has led to the increase in demand and production [2],[3].

Bioethanol is derived from lignocellulose biomass of tree trimmings, grasses, waste papers among others. These feed stocks contain lignocellulose, which includes lignin, hemicelluloses and cellulose, which when broken down could release fermentable sugar for biofuel production [4], [20].

Various treatment options are available for breaking down complex sugar into simple sugars; this can be done either through acidic hydrolysis at mild and high temperatures or through enzymatic hydrolysis which is another important treatment option [5], [6]. Our research interest explores cellulosic bioethanol production from sawdust of different wood origin. We will basically be focus on softwood sawdust of Ako tree and hardwood sawdust of Mahogany as the case study. Lignocellulose, the major component of the walls of plant cell, is mostly made up of, hemicellulose (about 20–40%), cellulose (about 40–60% of the total dry weight) and lignin (about 10–25%) [7], [8]. The major obstacle in the hydrolysis reaction of cellulose from lignocellulose biomass to produce fermentable sugars lies in isolating it from lignin those bonds with it making it difficult to expose to hydrolysis agent. In this work, we will study the effect of acid concentration on lignocellulosic content of different sawdust (softwood and hardwood) to yield fermentable sugar [9], [10].

Pretreatment is an expensive separation process, responsible for nearly 33% of the overall cost of bioethanol production [6]: the economic process needs to be evaluated and dually improved if the system could be viable [11], [12].

Lignin components of hardwood (20-25%) and for softwood (30-60%) are of importance to this research due to the dilution impact on the processes of fermentation and hydrolysis reactions [13], [14]. And thus, the procedure adopted in this research for pretreatment process, strictly addresses the economic needs as well as the release of microbial inhibitors that could possibly reduce the bioethanol yield. As earlier discussed, different pre-treatment options are available; this research will explore acidic hydrolysis by varying concentration of acid. This procedure will help achieve the targeted goal of high sugar yield in a way that other pretreatment methods may be limited. Acidic hydrolysis is characterized by breaking down of sugar into different by products like levulinic acid, 5-hydroxy-methyl-furfural, furfural and xylose [17], [18].

## 2 Materials and Methods

In this investigation, lignocellulose biomass (sawdust) of particle size 2.00mm was used; Sample A: Hardwood sawdust (Mahogany), Sample B: Softwood sawdust (Ako), Sample C: Mixed Sawdust of Hardwood /Softwood, bio-digester, digital PH meter, High Powered Liquid Chromatography (HPLC), Spectrophotometer, wild yeast isolated from rotten Oranges.

### 2.1 Sawdust Hydrolysis at varied Acid Concentration.

The pretreatment investigation using acid was carried out in a volumetric flask of volume 250 ml. The sawdust from Hardwood, Softwood and mixed Sawdust were labeled as Sample A, B and C respectively. After that the samples were soaked in 1M H<sub>2</sub>SO<sub>4</sub> at a

moderate reaction temperature of 80 °C this is for hydrolysis reaction to take place. Water Bath Thermostat was used for the reaction to ensure that uniform treatment was obtained and diffusion of acid into the chips was not a rate-limiting factor. This procedure was repeated for acid concentrations of 1.5M, 2M, 2.5M and 3M at a reaction time of half an hour on a water bath. After the duration elapsed, the lignocellulose biomass and liquids were separated using Whatman (mesh screen) No.1 filter paper. The hydrolysate which is the liquid fraction was isolated and stored for sugar analysis using High Power Liquid Spectrophotometer. The Filtrate and Residue after acidic hydrolysis reaction are shown in figure 1 a-d.



(a) Hydrolysate after hydrolysis reaction

(b): mixed sawdust after hydrolysis reaction



(c): Hardwood sawdust after hydrolysis reaction

(d): Softwood sawdust after hydrolysis reaction

**Figure 1:** Filtrate and Residue after acidic hydrolysis reaction

### 2.2 Acidic Hydrolysis Reaction of Lignocellulose Biomass

Acidic hydrolysis was preferred over enzymatic hydrolysis for this research work because of its ability to attack cellulose and hemicellulose fiber of lignocellulose biomass without being inhibited by lignin, therefore releasing higher amount of glucose. The major disadvantage of enzymatic hydrolysis is the poisoning of enzymes by lignin, which greatly impacts the reactive activity of enzyme leading to low glucose recovery [15], [16], [19].

Acidic hydrolysis reaction was studied at 80°C, using sulfuric acid at different concentrations; samples were withdrawn at a periodic interval of 15.0 minutes for measurement of glucose yield using High Power Liquid Chromatograph (HPLC).

### 2.3 Results from Acidic Hydrolysis of Lignocellulose Biomass

Following the design of experiment, the results in figure 2 a-e were obtained for 1M, 1.5M, 2M, 2.5M and 3M respectively for Hardwood sawdust, Softwood sawdust and mixed sawdust from different wood source.



**Figure 2:** Variation of glucose concentration with hydrolysis reaction time using 1M, 1.5M, 2M, 2.5M and 3M  $H_2SO_4$  respectively.

#### 2.4 Discussion of Results from Acid Hydrolysis of Lignocellulose Biomass

From Figure 2 a-e, there are three distinguish regions as the hydrolysis reaction proceeds. As a trend, region 1 (0 to 45 minutes) represent the lag phase, region 2 (46 to 75 minutes) represent the exponential phase, while region 3 (76 minutes to 120 minutes) represent degradation phase. At this region further sugar produced is been broken down into different by products like levulinic acid, 5-hydroxy-methyl-furfural, furfural and xylose.

On a general note, it was observed that as the concentration of sulfuric acid increases, glucose yield increases. As depicted in Figure 2 a-e for sawdust of Mahogany, as acid concentration increases from 1 M to 3 M, the yield of glucose increases from 47.30mg/ml to

54.49mg/ml. While for sawdust of Ako depicted in Figure 2 a-e, as the acid concentration increases from 1M to 3 M, the glucose yield increases from 49.82mg/ml to 54.61mg/ml. For mixed sawdust depicted in Figure 2 a-e, as the acid concentration increase from 1M to 3 M, the glucose yield increases from 49.56mg/ml to 55.89mg/ml.

Also, it was observed that at the course of reaction that the rate of sugar degradation raises with increase in concentration of acid. From Figure 2 a-e, it can be observed that for Hardwood, the glucose concentration decreased from 54.49mg/mL at 75 minutes of reaction to 51.00mg/mL after the duration of 120 minutes. Also, from Figure 2 a-e for Softwood, the concentration of glucose decreased from 53.22mg/mL at 90 minutes of reaction to 50.17mg/mL after reaction time of 120 minutes. While for mixed sawdust from Figure 2 a-e, the glucose concentration depreciates (decreased) from 55.89mg/mL at 90 minutes of reaction to 55.20mg/ml after reaction time of 120 minutes.

From Figure 2 a-e (at 1 M concentration of acid), it was observed that the maximum (optimum) glucose yield for sawdust of Mahogany is 47.30mg/mL after a reaction time of 120 minutes, whereas Ako is 49.82mg/mL after 105 minutes reaction time and 49.56 mg/mL after 105 minutes for mixed sawdust from different trees.

Clearly, the condition under this reaction favors sawdust of Ako tree at 49.82mg/mL, followed by mixed sawdust at 49.56mg/mL after the same reaction time.

From Figure 2 a-e (concentration of acid at 1.5 M), it was observed that the optimum glucose yield for sawdust of Mahogany is 55.21mg/ml after a reaction duration of 90 minutes, while that of Ako is 53.22mg/mL after 90 minutes of reaction and 56.38 mg/mL after 90 minutes for mixed sawdust from different trees.

Clearly, the condition under this reaction favors mixed sawdust of different tree at 56.38mg/mL, followed by sawdust of Mahogany at 55.21mg/mL after the same reaction time.

From Figure 2 a-e (2 M acid concentration), it was observed that the optimum glucose yield for sawdust of Mahogany is 56.82mg/mL after a reaction time of 90 minutes, while that of Ako is 52.93mg/mL after 105 minutes of reaction and 55.89L after 105 minutes for mixed sawdust from different trees.

Clearly, the condition under this reaction favors sawdust of Mahogany tree at 56.82mg/mL, followed by mixed sawdust of different trees at 55.89mg/mL after reaction time of 105 minutes.

From Figure 2 a-e (2.5 M of acid concentration), the optimum glucose yield for sawdust of Mahogany is 60.21mg/mL after a reaction duration of 105 minutes, while that of Ako is 59.48mg/mL after 105 minutes of reaction and 59.74L after 105 minutes for mixed sawdust from different trees.

Clearly, the condition under this reaction favors sawdust of Mahogany tree at 60.21mg/mL, followed by mixed sawdust of different trees at 59.74mg/mL after reaction duration of 105 minutes.

From Figure 2 a-e (3 M of acid concentration), the optimum glucose yield for sawdust of Mahogany is 54.49mg/mL after a reaction duration of 75 minutes, whereas Ako is 54.61mg/mL after 90 minutes of reaction and 55.89L after 90 minutes for mixed sawdust from different trees.

Clearly, the condition under this reaction favors sawdust of Mahogany tree at 54.489g/mL after reaction duration of 75 minutes, closed by is mixed sawdust of different trees at 55.89mg/mL after reaction time of 90 minutes.

## 2.5 Kinetic Model for Hydrolysis Reaction of Lignocellulose Biomass

The model representing lignocellulose biomass involves a series of pseudo-homogeneous irreversible first-order reactions. The decomposition reactions were negligible in this research as the operating media were not favorable for degradation of glucose. Table 1-3 show the glucose yield with time, while figure 3 a-c are the corresponding reaction rate plot.

**Table 1:** Hardwood at  $PH = 2.5M, C_o = 70mg/mL$   $weihgt = 100g, X =$  sugar concentration  $mg/ml$ .

$t, minutes$	$X(mg/mL)$	$C_o - X(mg/mL)$	$\frac{C_o}{C_o - X}$	$\ln\left(\frac{C_o}{C_o - X}\right)$
0.00	0.00	70.00	1.000	0.000
15.00	12.24	57.76	1.212	0.192
30.00	23.08	46.92	1.492	0.400
45.00	31.58	38.42	1.822	0.600
60.00	39.87	30.13	2.323	0.843
75.00	46.94	23.06	3.036	1.110
90.00	54.38	15.62	4.481	1.500
105.00	60.21	9.79	7.150	1.967
120.00	58.35	11.65	6.009	1.793

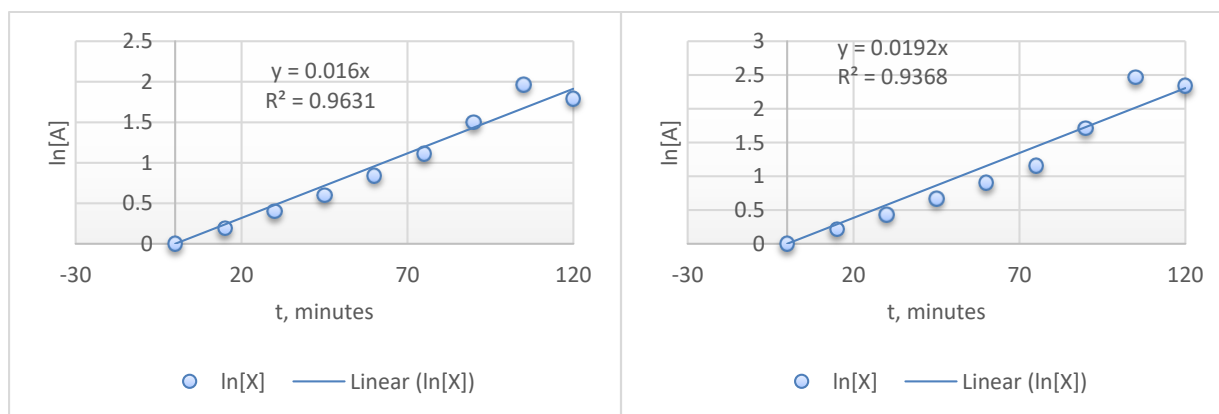
**Table 2:** Softwood at  $PH = 2.5M, C_o = 65mg/mL, weihgt = 100g$

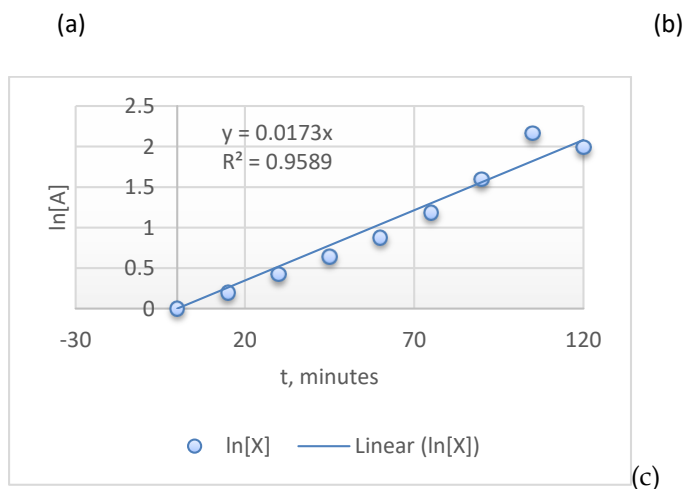
$t, minutes$	$X(mg/mL)$	$C_o - X(mg/mL)$	$\frac{C_o}{C_o - X}$	$\ln\left(\frac{C_o}{C_o - X}\right)$
0.00	0.00	65.00	1.000	0.000
15.00	12.90	52.10	1.248	0.221
30.00	22.88	42.12	1.543	0.434
45.00	31.73	33.27	1.954	0.670
60.00	38.63	26.37	2.465	0.902
75.00	44.63	20.37	3.191	1.160
90.00	53.32	11.68	5.565	1.717
105.00	59.48	5.52	11.775	2.466
120.00	58.73	6.27	10.367	2.339

**Table 3:** Mixed Sawdust at  $PH = 2.5M, C_o = 67.5 mg/mL, weihgt = 100g$

$t, minutes$	$X(mg/mL)$	$C_o - X(mg/mL)$	$\frac{C_o}{C_o - X}$	$\ln\left(\frac{C_o}{C_o - X}\right)$
0.00	0.00	65.5	1.000	0.000
15.00	11.98	55.52	1.216	0.195
30.00	23.23	44.27	1.525	0.422
45.00	32.05	35.45	1.904	0.644
60.00	39.36	28.14	2.399	0.875
75.00	46.87	20.63	3.272	1.185
90.00	53.85	13.65	4.945	1.598
105.00	59.74	7.76	8.698	2.163
120.00	58.30	9.20	7.337	1.993

Plotting the graph of  $\ln\left(\frac{C_o - X}{C_o}\right)$  against  $t$ , we could obtain the value of specific rate constant,  $k$ .





**Figure 3:** Kinetics plot for Mixed Sawdust at 2.5M for Hardwood, Softwood and mixed sawdust respectively.

### 2.6 Discussion of Kinetic Parameters for Hydrolysis Reaction

From Figure 3 a-c, the hydrolysis reaction of Softwood is the fastest at  $0.0192\text{min}^{-1}$  (Figure 3b) that is closely followed by mixed Sawdust at  $0.0173\text{min}^{-1}$  (Figure 3c) and Hardwood sawdust is the least at  $0.0160\text{min}^{-1}$  (Figure 3a). The result is not surprising because; the amount of activation energy required for hydrolysis of Hardwood sawdust was 1.2 times higher comparing with others. Using Softwood Sawdust as a standard the ratio of activation energy to other lignocellulose biomass used for this experiment was 1:1 and 1:2 for mixed sawdust and Hardwood sawdust respectively.

### Conclusion

After careful analysis of the results of this research, the following points and conclusions were drawn:

1. Hydrolysis reaction medium of 2.5M sulphuric acid and temperature of  $80^{\circ}\text{C}$  gave the optimum sugar recovery for the samples involved: 60.21mg/ml, 59.48mg/ml and 59.74mg/ml for sawdust of Mahogany, Ako and Mixed sawdust respectively.
2. The kinetic parameters of hydrolysis reaction indicate a fast reaction rate for all the three samples. The specific rate constant for Hardwood, Softwood and mixed sawdust were 0.016, 0.019 and 0.017 respectively.

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