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Kinetic Study on Hydrolysis of Cellulosic Waste Saw-Dust into Glucose using Hydrochloric and Sulphuric Acids

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ABSTRACT: This research paper studied the kinetics of hydrolysis of cellulose to glucose using two major inorganic acids (Hydrochloric and Sulfuric) at constant temperature of 80^{o}C. The steps employed to achieve this involved extraction of cellulose from sawdust and saccharification (hydrolysis) of starch to simple sugar (glucose). The glucose concentration gotten from each acid hydrolysis was analyzed to know the acid among the two that is better cellulose saccharification. It was observed that Hydrochloric acid hydrolyzed more than the Sulphuric acid. This is evidenced from the fact that the maximum absorbance and glucose concentration for HCl is 1.244 and 0.128 respectively while the Absorbance and glucose concentration for H_2SO_4 is 0.887 and 0.094 respectively. Finally, sugar analysis was carried out to determine the acid with the highest yield of glucose and the best acid for the hydrolysis. It was noticed that the yield of glucose was relatively high from HCl at 1.280% concentration, followed by H_2SO_4 at 0.940%. It was also seen from the graph that the absorbance yield increases as the glucose concentrations increases in terms of HCl. Therefore, the best acid for acid hydrolysis of saw-dust is HCl.

KEYWORDS: Acid hydrolysis, cellulose, sawdust, kinetics, Hydrochloric acid and Sulphuric acid.

I. INTRODUCTION

Vast quantities of waste materials and by-products from various sources are generated from the manufacturing process, service industries and municipal solid waste. As a result, solid waste management has become one of the major environmental concerns in the world (Abdul Awal et al., 2016). With the increasing awareness of the environment protection and biomass regeneration, significant research has been going on globally on the utilization of waste materials and by-products (Siddique R, 2008). Recycling of such wastes into new materials could be a viable solution to the pollution problem (Chandra S, 1997; Udoeyo and Dashibil, 2002

In these recent years, the interest of the research in the cellulose based-materials has been increasing due to the demand for the renewable resources and growing on environmental awareness (Mohanty, et al.,2005).. Conner et. al, (1986) noted that Pyrolysis, gasification, liquefaction, and saccharification (hydrolysis) of cellulosics have all been proposed as methods for utilizing renewable biomass as an energy or chemical source. Natural cellulose fibers become greater in being used as one of the materials in thermoset and thermoplastics polymeric matrices instead of glass fibers because of their characteristics which are renewability, low density and high specific strength. The excellent characteristics of the cellulose which include the biodegradability and the capacity for the broad chemical modification increased the interest and encourage the worldwide research on cellulose over the past few decades. (Festucci-Buselli et. al., 2007; Sun et. al., 2009; Voitl, et. al., 2010; Wang et. al., 2011; Tolba et. al. 2015; Varanasi, et. al., 2015). There are several plants such as cotton, wood, bamboo, flax, hemp, sisal, and jute that are rich in cellulose.

Sawdust (or wood shavings) is a by-product or waste product of woodworking operations such as sawing, milling, planing, and routing (Baran and Teul, 2007). According to Rominiyi et al., (2017), it is a tiny piece of wood that fall as powder from wood as it is cut by a saw. It is also an industrial waste obtained as by-

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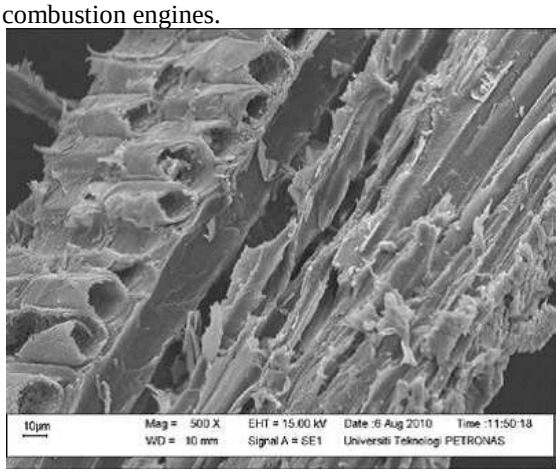
products from cutting, sawing or grinding of timber in the form of fine particle (Abdul Awal et al., 2016). Wood dust is also the byproduct of certain animals, birds and insects which live in wood, such as the woodpecker and carpenter ant (Baran and Teul, 2007). It is composed of small chippings of wood. These operations can be performed by woodworking machinery, portable power tools or by use of hand tools. In some manufacturing industries it can be a significant fire hazard and source of occupational dust exposure. In other words, sawdust is basically a waste of small

particles available in saw-milling industries, pulp plant and paper industries as well as wood processing industries particularly, in the southern part of Nigeria in a quite large volume in form of heaps and mostly burnt off resulting in the environmental pollution (Adegoke and Mohammed, 2002). Sawdust is generally considered as a timber-industrial waste that pollutes the environment (Alexandru, R.S. 2002; Phonphuak and Chindapraist, 2015) but can become a valuable commodity either as a raw material in manufacturing industries for wood boards, light construction materials such as shelves, notice boards, wall and roof sheeting for mobile houses, as an insulator in the refrigerating system and cold conservation of in Energy industries as fuel burned directly or indirectly to produce wood gas, briquette, pellet, etc. Rominiyi et al., (2017) further noted that Sawdust that ordinarily constitutes a menace in sawmills is a good source of fuel, biogas, animal feed meal, organic manure, weed killer and particle board and briquettes. The flame-purified gas is found useful to power internal combustion engines.



II. SCANNING ELECTRON MICROGRAPH (SEM) OF SAWDUST PARTICLES

Cellulose is one of the major constituent of all plant materials, which formed about half to one-third of all plant tissues and constantly fill up again by photosynthesis process. According to (Mari Granström, 2009; Festucci-Buselli et. al., 2007), the most abundant lignocellulosic resource on Earth is wood. The main chemical components of sawdust are carbon (60.8%), hydrogen (5.2), oxygen (33.8%), and nitrogen (0.9%) (Phonphuak and Chindapraist, 2015). Wood is primarily composed of macromolecular substance with 40-50% cellulose, 15-25% hemicellulose, lignin 15-30% and minor amounts (5-10%) of extraneous materials (Adeeyo et al., 2015; Phonphuak and Chindapraist, 2015). (Kim et al., 2012; Adeeyo et al., 2015; Amanullah et al, 2013; Wan SulwaniIzzatibinti Wan BaderulHisan et al. 2017). Cellulosic materials are sometimes called lignocellulosic materials due to their lignin, hemicellulose, and cellulose composition.

Hydrolysis of cellulose is the process of breaking the glucosidic bonds that holds the glucose basic units together to form a large cellulose molecule. It is a term used to describe the overall process where cellulose is converted into various sweeteners. Hydrolysis is a chemical reaction during which one or more water molecules are split into hydrogen and hydroxide ions, which may go to participate in further reactions (Dussán et al,. 2014)

Although cellulose possesses excellent strength and good stability, yet it can be degraded by resorting to a variety of chemical and physical processes under certain conditions (Fan et al, 1987). The most common manifestation of its deterioration is a decrease in the average degree of polymerization (DP). Usually this deterioration is accompanied by a chemical modification of the cellulose molecule, such as an increase in its reducing power or development of reactive groups along the chain (McBurney LF 1954). When cellulose is hydrolyzed in an acidic medium to glucose, the P-l,4-glucosidic bonds of a cellulose chain molecule are split by the addition of water molecules; this addition yields fragments of shorter chain lengths while preserving the basic structure. One of the newly formed end-groups of chain molecules is a potential aldehyde group possessing reducing power (Wenzl HFJ 1970).

Hydrolysis of cellulose with concentrated acid proceeds through the formation of cellulose acid complexes; this occurs only after the crystalline structure of cellulose is destroyed by its dissolution or swelling in acid (Goto K et al. (1971); Whalley E (1959))

Cellulose - acid complex - oligo saccharides - glucose

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$(C_6H_{10}O_5.4H_2O.\ H_2SO_4)n$ with sulfuric acid
$(C_6H_{10}O_5.4H_2O.\ HCl)n$ with hydrochloric acid
$(C_6H_{10}O_5.4H_2O.\ H_3PO_4)n$ with phosphoric acid
$(C_6H_{10}O_5\bullet H20.\ HNO_3)n$ with nitric acid

Acid concentration significantly influences the kinetics and course of hydrolysis (Fan et. al., 1987). In 40 % hydrochloric acid, the cellulose is degraded only to oligo saccharides at about 30°C. The oligo saccharides are hydrolyzed to glucose according to a first-order mechanism only at a higher temperature.

Hydrolysis of cellulose with hot dilute acid proceeds through the formation of hydro cellulose to soluble polysaccharides and then to simple sugars, i.e.,

native cellulose → stable cellulose (hydrocellulose) → soluble polysaccharides → glucose

In this serial reaction, the rate-controlling step is hydrolysis of stable hydrocellulose to soluble polysaccharides (Fan, et al. 1987)

III. MATERIALS AND METHOD

The saw-dust (cellulose) used in this research work was sourced from Afikpo Timber Shade, Afikpo North Local Government Area, Ebonyi State, Nigeria while the apparatus used for the research include: Burette, Wooden stand, 250 ml beaker (x 6), 5 ml syringe, Test tube (x 5), Temperature Water bath (Large beaker + Bunsen burner), Stopwatch, Cuvette, Cotton bud, Funnel, Filter paper, Visible spectrophotometer, Pipette, Industrial paper, Spatula, Weighing balance, Filter holder

A. Hydrolysis (Acid Hydrolysis)

Firstly, the sawdust obtained was pretreated physically with the use of a blender in order to reduce the size of the sawdust and ultimately, the surface area of the material. 10g of saw-dust was weighed and mixed with 100ml of distilled water; it was poured into a beaker and was stirred thoroughly. The mixture of saw-dust and water was put into a heating mantle for one hour at a constant temperature of 80^OC. Then 10ml of 18M Hydrochloric acid was then added to the sawdust in the beaker. The sample was heated again for another one hour. Following this, the pH of the sawdust, acid and water mixture was taken with the pH meter. Potassium hydroxide (KOH) solution was added to the solution with a dropper bottle until the pH was in the desired range of between 5.0 and 6.0. This procedure was repeated for 18M Hydrochloric acid of 20ml, 30ml, 40ml, 50ml and 18M sulfuric acid of volume 10ml, 20ml, 30ml, 40ml and 50ml.

B. Determining The Glucose Content

The glucose content that was present in the hydrolyzed sawdust was determined with the use of Dinitrosalicylic reagent (DNSA) by method Ranken (1984) and a spectrophotometer.

C. Preparing The Dnsa Reagent

The DNSA reagent was prepared by adding 20ml of 2N NaOH to 1g of dinitrosalicylic acid (DNSA) in order to dissolve the DNSA. Then, 50ml of distilled water was used to dissolve 30g of Rochelle salt (NaK tartrate). The NaK tartrate solution was then added to the DNSA solution and the mixture was made up to 100ml with distilled water.

D. Obtaining The Standard Glucose Curve

Different concentrations of glucose ranging from 0.01mg/ml to 0.1mg/ml were prepared. 2ml of the DNSA reagent then added to 1ml of the different glucose concentrations. The mixture was heated for 5mins over a water bath, and then cooled in cold water. The absorbance of the sample was obtained with the use of the spectrophotometer at a wavelength of 540nm. The glucose concentration is plotted against the absorbance to obtain a standard curve as show in Figure 1.

E. Obtaining The Glucose Content

2ml of the DNSA reagent was added to 1ml of a sample. The mixture was heated for 5 mins over a water bath, and then cooled in cold water. The absorbance of the sample was then obtained with the use of the spectrophotometer at a wavelength of 540nm. The glucose concentration was obtained with the use of the standard curve.

IV. RESULTS AND DISCUSSION

A. RESULTS

The tables below shows the results obtained from glucose analysis and glucose yield with HCl, and H_2SO_4, at different concentration. Figure 4.1, 4.2 and 4.3 shows the graph of sugar percentage (%) yield with various acids. The detailed calculations are showed in the appendices. This results obtained in the experiments carried out are presented in both tabular and graphical forms.

B. DISCUSSION

From the results, the rate of hydrolysis is greatly influenced by acids and their concentrations. This is in accordance with Fan et. al.,(1987). These concentrations also greatly affect the glucose yield produced by the individual acids. Increase in concentration of acids enhances the

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hydrolysis process positively, as the cellulose hydrolyzed more with increase in concentration of acid as shown in Figure 2 and 3 for both H_2SO_4 and HCL respectively. This is in accordance with (Adeeyo et al., 2015) that acid hydrolysis is a requisite for the breakdown of the cellulose bonds. However, HCL is a better acid than sulphuric acid in cellulose acid hydrolysis.

From tables 2 and 3, it was observed that the optimal yield of H_2SO_4 and HCl were (0.940) and (1.280) respectively. The results obtained from the same tables as mentioned above also showed that HCl has relatively higher absorbance (1.280) yield at 1.244g than H_2SO_4 whose yield is 0.940 at 0.887g. From figure 4, it can be seen that when both inorganic acids are compared, HCl has a better yield than H_2SO_4. This goes to show that H_2SO_4 takes more time in breaking down the glucosidic bond of cellulose.

V. CONCLUSION

This research work has shown that it possible and economically viable to use lignocellulose material such as saw-dust for industrial sugar production through acid hydrolysis. However, the yield of glucose from hydrolyzed cellulose is affected by various acids HCl and H_2SO_4 as well as their concentrations. It was observed that the higher the concentration of both acids, the higher the simple sugar yields. For this research, the highest yield of glucose was obtained at 50ml for both acids with HCl yielding the most.

TABLE 1: VARIATION OF ABSORBANCE WITH THE STANDARD GLUCOSE CONCENTRATION.

STANDARD GLUCOSE CONCENTRATION (g)	ABSORBANCE (540nm)
0.01	0.095
0.02	0.190
0.03	0.282
0.04	0.374
0.05	0.463
0.06	0.834
0.08	1.032
0.10	1.153

TABLE 4.2: VARIATION OF ABSORBANCE WITH SULPHURIC ACID

Sulphuric acid(H_2SO_4)	Absorbance	Glucose concentration(g)	Percentage (%) yield
10ml	0.233	0.025	0.250
20ml	0.394	0.042	0.420
30ml	0.553	0.059	0.590
40ml	0.743	0.079	0.790
50ml	0.887	0.094	0.940

TABLE 4.3: VARIATION OF ABSORBANCE WITH HYDROCHLORIC ACID

Hydrochloric acid (HCl)	Absorbance	Glucose concentration(g)	Percentage (%) yield
10ml	0.220	0.024	0.240
20ml	0.481	0.052	0.520
30ml	0.724	0.076	0.760
40ml	0.982	0.105	1.050
50ml	1.244	0.128	1.280

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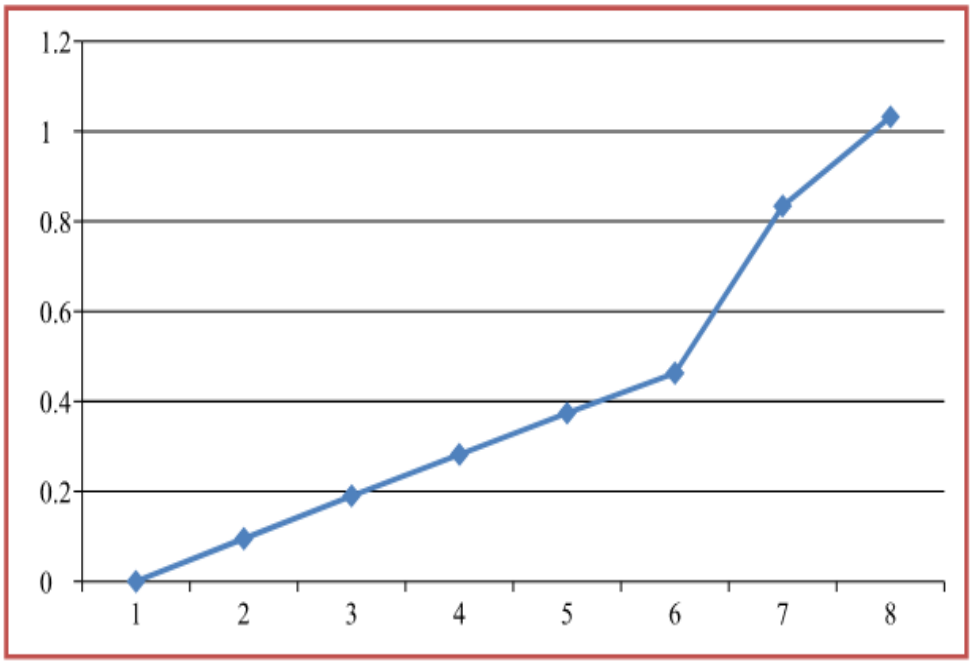

FIG. 1: ABSORBANCE (540M) VS STANDARD GLUCOSE (G): STANDARD GLUCOSE CURVE

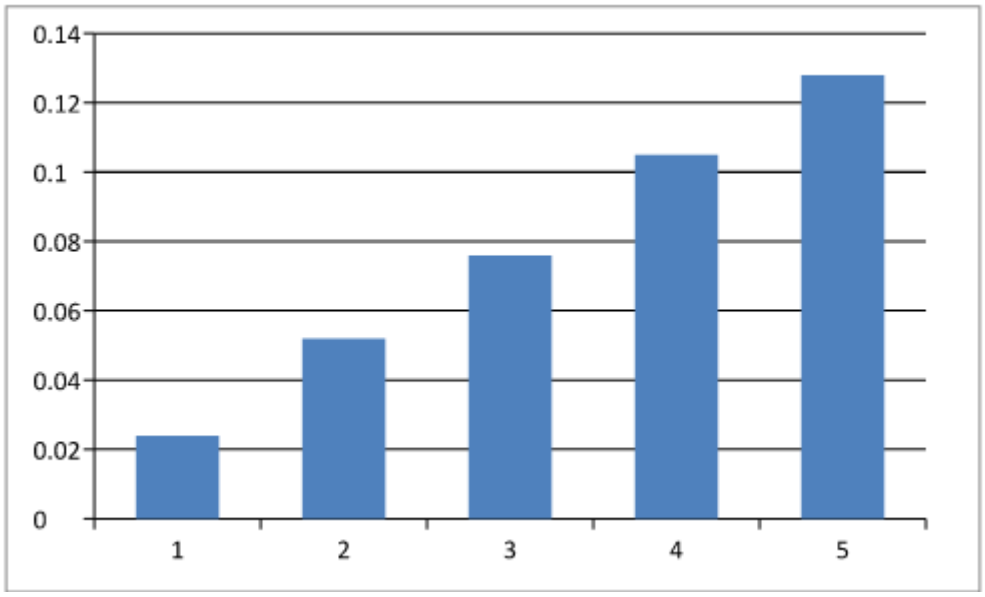

FIG. 2: VOL. OF H_2SO_4 ACID VS GLUCOSE CONCENTRATION

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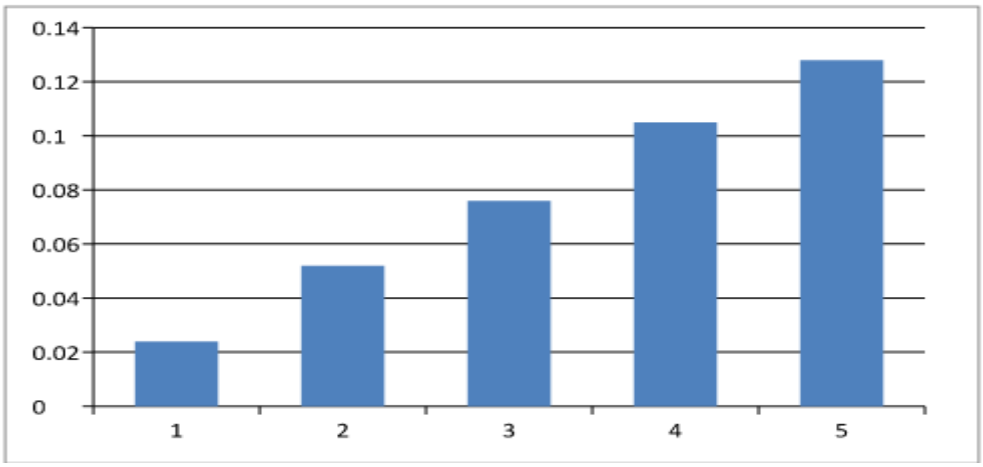

FIG. 3: VOL. OF HCL ACID VS GLUCOSE CONCENTRATION

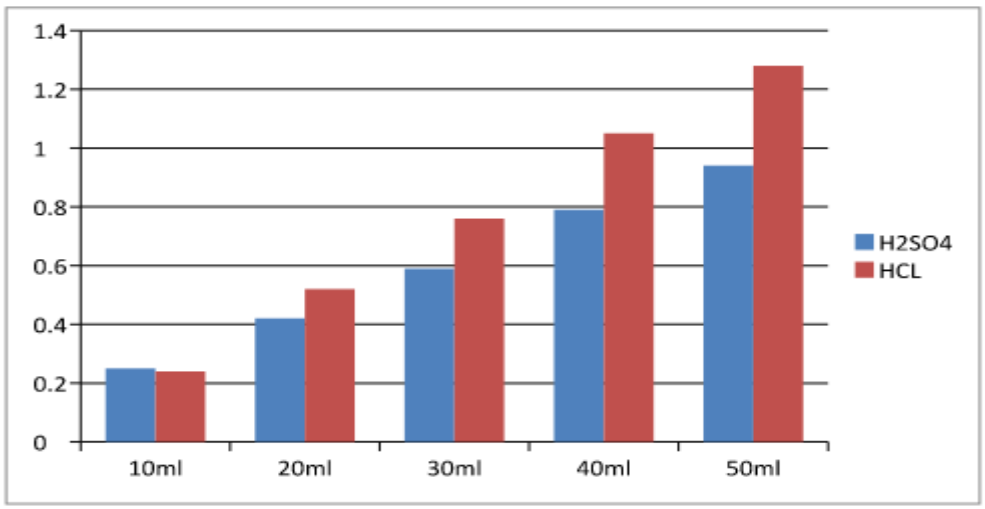

FIG. 4: % YIELD OF GLUCOSE FOR H_2SO_4 AND HCL AT THE SAME VOLUME.

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