

THE KINETIC STUDY ON HYDROLYSIS OF CELLULOSE (SAW-DUST)

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CERTIFICATION

This project report on the topic of the kinetic study of hydrolysis of cellulose (saw-dust) using hydrochloric acid was written and compiled by Nwafor Nwamaka Loveth with registration number CHE/2007/079 in partial fulfillment of the requirement for the award of a bachelor of Engineering (B.ENG) degree in Chemical Engineering has been approved by the undersigned.

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DEDICATION

This project is dedicated to the Almighty God who had made it possible for me to survive throughout my stay in school. My blessed mother Mary, the powerful intercessor, the Holy Spirit, giver of wisdom. My parent (Mr. and Mrs.) Nwafor, brothers, sister and to my friends for giving me the privilege and support in writing this project.

ACKNOWLEDGEMENT

This research project would not have been possible without the genuine and selfless assistance of those who contributed in no small measure to make it a success.

My immense gratitude and praise goes to God almighty for his mercy, kindness, strength, numerous blessing and for the successful completion of my studentship in Caritas University Emene Enugu .

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ABSTRACT

This research project studied on the kinetics of hydrolysis of cellulose to glucose. The steps employed to achieve this project involved extraction of cellulose from sawdust and subsequently, hydrolysis of starch to simple sugar. This was followed by glucose analysis. Different experiments were conducted during acid hydrolysis to study the various acids on the hydrolysis of cellulose to glucose. The saw-dust was extracted from the wood by grinding using saw. The process used in the hydrolysis was acid hydrolysis in which two major inorganic acids (Hydrochloric and Sulfuric) were used at constant temperature of 80°C. During this experiment, it was observed that Hydrochloric acid hydrolyzed most, followed by Sulphuric acid. 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 H₂SO₄ 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 is HCl.

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CHAPTER ONE

1.1 INTRODUCTION

Cellulose is a naturally occurring polymeric material containing thousands of glucose-like rings each of which contain three alcoholic OH groups. Its general formula is represented as $(C_6H_{10}O_5)_n$. The OH-groups present in cellulose can be esterified or etherified, the most important cellulose derivatives are the esters. Cellulose is the name given to a long chain of atoms consisting of carbon, hydrogen and oxygen arranged in a particular manner. Cellulose is found in nature in almost all forms of plant life, and especially in cotton and wood. A cellulose molecule is made up of large number of glucose units linked together by oxygen atom. Each glucose unit contains three(3) Hydroxyl groups, the hydroxyl groups present at carbon-6 is primary, while two other hydroxyl are secondary. Cellulose is the most abundant organic chemical on Earth more than 50% of the carbon in plants occurs in the cellulose of stems and leaves. Wood is largely cellulose, and cotton is more than 90% cellulose. It is a major constituent of plant cell walls that provides strength and rigidity and prevents the swelling of the cell and rupture of the plasma membrane that might result when osmotic conditions favor water entry into the cell. Cellulose is a fibrous, tough, water-insoluble substances, it can be seen in cell walls of plants, particularly in stalks, stems, trunks and all woody portions of the plant.

Cellulose is polymorphic, i.e there are a number of different crystalline forms that reflect the history of the molecule. It is almost impossible to describe cellulose chemistry and biochemistry without referring to those different forms. Cellulases are gotten from cellulose, cellulose is also found in protozoa in the gut of insects such as termites. Very strong acids can also degrade cellulose, the human digestive system has little effect on cellulose. The word cellulose means β -1,4-D-glucan, regardless of source because of the importance of cellulose and difficulty in unraveling its secrets regarding structure, biosynthesis, chemistry, and other aspects, several societies are dedicated to cellulose, lignin, and related molecules.

1.2 SOURCES OF CELLULOSE

Cellulose for industrial conversion comes from wood and scores of minor sources such as kenaf paper and rayon are now made mostly from wood pulp. cotton rings were historically important for paper making, and cotton linters (short fibres are used to spin yams) are now used in high quality writing and currency papers.

Cellulose forms very tightly packed crystallites, these crystals are sometimes so tight that neither water nor enzymes can penetrate them; cellulose consists of two cellulose molecules;

Crystalline and amorphous cellulose. The crystalline cellulose is insoluble because of the inability of water to penetrate cellulose, On the other hand amorphous cellulose allows the penetration of endoglucanase, another subgroup of cellulase that catalyze the hydrolysis of internal bonds. The natural consequences of this difference in the crystalline structure is that the hydrolysis rate is much faster for amorphous cellulose than crystalline cellulose.

Some cellulose comes from the hairs (trichomes) on seeds, example: cotton, kapo and milk weed. A commercial bacterial cellulose product (cellulon) was introduced by Weyerhaeuser(22) for use in foods, the product is called primacel and is available from Nutrasweet kelco. Recently, cellulose from sugar belt pulp and from citrus pulp has aroused interest for use as a fat substitute.

1.3 HYDROLYSIS

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.

1.4 SUGAR

Sugars (also called saccharides) are compounds containing an aldehyde or ketone group and two or more hydroxyl groups. Sugar can also be a sweet crystalline substance obtained from sugar-cane and sugar beet. It includes sucrose, glucose and fructose.

1.5 STATEMENT OF THE PROBLEM

The clamour for the diversification of Nigerian economy through low quality products has motivated researchers to explore the numerous domestic, industrial and economic importance of one Nigeria's major product (cellulose) which forms the bedrock of this project.

Sugar is a commodity of high demand for both domestic and industrial applications on daily basis in homes, small and medium scale industries e.t.c. this is why Nigeria government spends huge sums of money on importation of sugar and sugar products to meet the demand of citizens. Among the many processes of sugar production, is acid hydrolysis of (cellulose) has proved to be a process which encourages the production of high quality with minimum skill and materials. This work is therefore an effort to encourage industrialists, researchers, and students to carry out more intensive studies on production of sugar from cellulose for production of sugar and enhanced economic resources for the nation.

1.6 RELEVANCE OF THE STUDY

Nigeria is the largest producer of cellulose for which paper wood is made. A large percentage of produced cellulose is consumed as paper, textiles, newspaper and containers in form of writing, reading e.t.c.

The method of acid hydrolysis of cellulose:

- It creates job opportunities, hence, reducing unemployment in the country.
- It helps to know the best acid for the hydrolysis of cellulose.
- It establishes the industries for government to contribute immersely towards the country economy.
- With the methods of glucose and cellulose production, the cost of glucose and cellulose will reduce.
- It produces research workdone on the digestion of cellulose into glucose which I will engage on it after my graduation.

1.7 OBJECTIVES.

The research project covers the processes, operations and pathways involved in the Acid hydrolysis of cellulose to produce (glucose) sugar. The research study aims at:

- Quantifying and calculating the yield of glucose from the hydrolysis of cellulose using two different acids.
- The hydrolysis of cellulose into sugar using different concentration of hydrochloric acid and sulphuric acid.

CHAPTER TWO.

2.0 LITERATURE REVIEW

Cellulose is a main structural element providing strength and structure to all plant organs. It is one of the essential 'LEGO' bricks of nature. The structure of cellulose is quite unique it is build up from the simple sugar glucose to form a linear polymer of glucan chains organized into micro fibrils. It is the component of the primary cell wall of green plants, many forms of algae and the oomycetes some species of bacteria secrete it to form biofilms.

Cellulose is the most common organic compound on earth with the structural formula $(C_6H_{10}O_5)_n$ it is a polysaccharide that consist a linear chain of several hundred to over ten thousand $\beta(14)$ linked D-glucose units. Cellulose is obtained from cotton, it is mainly used to produce paper board, textiles, containers and paper to a smaller extent it is converted into a wide variety of derivative products such as cellophane and rayon converting cellulose from energy crops into biofuels such as cellulose ethanol is under investigation as an alternative fuel source.

Cellulose is used to make water-soluble adhesives and binders such as methyl cellulose and carboxy methyl cellulose which are used in wallpaper paste. Cellulose is the raw material in the manufacture of nitro cellulose (cellulose nitrite) which is used in

smokeless gun powder and as the base material for celluloid used for photographic and movie films until the mid 1930s.

Laboratory Isolation of Cellulose is used as the stationary phase for thin layer chromatography. Cellulose is further used to make hydrophilic and highly absorbent sponges. Cellulose fibres are also used in liquid filtration. Cellulose Insulation made from recycled paper is becoming popular as an environmentally preferable material for building insulation. It can be treated with boric acid as a fire retardant.

The most abundant organic compound on earth is cellulose, which provides the primary structural component for plants. (Chitin, present in insects, crustacean, and bones, is the second most abundant organic compound.) Like starch, cellulose is a polymer of glucose monomer units, linked together at the beta-1,4 locations as opposed to the alpha-1,4 locations for amylose (insoluble starch). Enzymes are generally extremely specific in their catalytic actions. They can recognize even the subtlest difference in the substrate structure and often exhibit no measurable catalytic behavior toward other similarly structured substrates. The difference in the glucose linkage between starch and cellulose makes it impossible for the starch digesting enzymes, e.g. alpha-amylase, to break down cellulose. The direct consequence of this specificity is that various organisms, including humans, cannot use cellulose to satisfy their nutritional requirement for carbohydrates. However, some animals and insects, such as cattle, sheep, horses, termites, and caterpillars, can subsist on wood and grass, although they themselves do not produce

cellulolytic enzymes. This is due to the synergistic effect of the bacteria present in their digestive tracts. These gut bacteria flora secrete the necessary cellulolytic enzymes to digest cellulose, and the hosts, in turn, provide them with a shelter as well as nutrient. The inability of most organisms in attacking cellulose is not necessarily undesirable. For example, wood, which is mostly cellulose bound together by lignin, has traditionally been used as building materials due to its relatively stable microscopic structures. Wouldn't it be terrible if your home could be digested by bugs too easily? Perhaps, that is why no one uses bread (starch material) or candy (easily digestible saccharides) to build a durable house except in fairy tales.

There has been a large amount of research work done on the digestion of cellulose into glucose. The generated glucose can be used to produce single cell protein as food for livestock or even for humans. Glucose can also be used as the starting raw material in the production of a wide variety of chemicals and fuels. This is usually carried out with the help of microorganisms. For example, glucose can be easily fermented to ethanol by *Saccharomyces cerevisiae* (yeast) or *Pseudomonas mobilis* (bacterium). Ethanol can be used as gasoline or processed further to make other common petrochemicals. Another example is the conversion of glucose into solvents such as acetone and butanol by *Clostridium acetobutylicum*. Because the volume of cellulose is so overwhelming and because the resource is renewable, the world will likely to depend on it more heavily for

food, fuel, chemical supplies, and raw materials in the future. It has the great potential of alleviating the need for petroleum, whose supply is fast dwindling.

Thus, the ability to manipulate this organic chemical has extremely important implications. A breakthrough in the investigation of cellulose digestion processes will not only have an enormous impact on the world food supply, economy, and geopolitical balance of power, it will also greatly influence the various types and ways products are produced by the chemical industry and enjoyed by the end users. This experiment introduces a student in biochemical engineering to one of tomorrow's technologies with the most far-reaching impacts.

As demonstrated in this experiment, the breaking down some of the cellulose is really not very difficult. However, translating a process from a laboratory scale to a commercial scale is not so trivial. First of all, the entire operation has to be *both* technically sound and economically feasible. In order for a process to be actually adapted, it, of course, has to be technically possible first. In addition, it must offer some clear advantage over all other competing processes. This advantage is almost always measured in the form of a larger profit margin, irrespective of the political system in which the process is to be employed. Note that in calculating the profit, one must duly include various costs that are sometimes not obvious nor easy to estimate, e.g. the public images, institutional responsibilities, and environmental impacts. Unprofitable processes are a waste of natural and human

resources and must not survive. As a chemical engineer, whether conducting basic research or designing a plant, one is continually reminded of the economical impact.

Two typical approaches to affect a similar end result are studied in this experiment.

However, one should keep in mind that there are numerous other competing approaches, and one is constantly faced with multiple choices. For example, acetic acid can be produced by fermentation means or chemical synthesis. So are a wide range of pharmaceuticals. As a matter of fact, life is rarely simple and straight forward enough that there is only one choice.

2.2 HISTORY OF CELLULOSE

Cellulose was discovered in 1838 by the French chemist Anselme Payen, who isolated it from plant matter and determined its chemical formula. Cellulose was used to produce the first successful thermoplastic polymer celluloid by Hyatt manufacturing company in 1870, Herman Staudinger determined the polymer structure of cellulose in 1920. The compound was first chemically synthesized (without the use of any biologically derived enzymes) in 1992, by Koba Yashi and Shoda.

Cellulose is insoluble in all ordinary solvents and may be readily separated from the other constituents of plants. Depending on its concentration, sulfuric acid acts on cellulose to produce glucose, soluble starch, or amyloid; the last is a form of starch used for the coating of parchment paper.

Cellulose esters are used in paper sizings, adhesives, soaps and synthetic resins.

2.3 OCCURENCES

Cellulose is mostly found in plants as microfibrils (1598). It usually forms the structurally strong framework in the walls. Cellulose (E460) is mostly prepared from wood pulp. Cellulose is made from sugar; it can also be processed to fuels and chemicals by microorganisms fermenting the sugar. Some example; the conversion of cellulose to second generation bio- ethanol by yeast or the production of bio-plastic based on lactic acid from bacteria.

2.4 ENERGY STORE OF PLANTS

In photosynthesis, plants use light energy to produce glucose from carbondioxide. The glucose is stored mainly in the form of cellulose granules; in plastids such as chloroplasts and especially amyloplasts.

The major combustible component of non food energy crops is cellulose; with lignin, second- non-food energy crops are more efficient than edible energy crops and which have a large starch component, but still compete with food crops for agricultural and water resources.

Typical non-food energy crops include industrial hemp, switch grass, miscanthus, salus (willow) and populous (popular) species.

Some bacteria can convert cellulose into ethanol which can then be used as a fuel; glucose is soluble in water, hydrophilic, binds much water and then takes much space, glucose in the form of starch on the other hand, is not soluble and can be stored much more compactly.

2.5 BIOSYNTHESIS OF CELLULOSE

Plants use light energy to produce glucose from carbon dioxide via a process known as photosynthesis. The glucose is stored mainly in the form of starch granules in plastids such as chloroplasts and especially amyloplasts.

Cellulose synthesis requires chain initiation and elongation; and the two processes are separate. A glucosyltransferase initiates cellulose polymerization using a steroid primer, sitosterol-beta-glucoside, and UDP-glucose.

Cellulose synthase utilizes UDP-D-glucose precursors to elongate the growing cellulose chain. A cellulase may function to cleave the primer from the mature chain. The biosynthesis of cellulose equally have major advances of understanding. Two areas are of interest, biochemistry and molecular biology

Biochemistry : There have been reasonable progress in the biochemistry of cellulose synthesis, but inherent difficulties lie in the isolation and characterization of the proteins that comprise the membrane bound terminal complex (TC) first described by Brown and Montecrios (26).

Some of the most important advances in cellulose biosynthesis have originated from the combined areas of molecular biology and molecular genetics.

2.6 STRUCTURE OF CELLULOSE

Cellulose is derived from D-glucose units, which condense through β (1-4) glucosidic bonds. This linkage motif contrasts with that for α (1-4) glucosidic bonds present in starch, glycogen, and other carbohydrates. Cellulose is a straight chain polymer: unlike starch; no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose form one chain from hydrogen bonds with oxygen atoms on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength.

The structure of cellulose is simple linear polymers of thousands of β (1-4) linked D-glucose units, assembled into bundles of about 36 chains, which aggregate side by side to form a microfibril.

Each year, worldwide, plants synthesize more than 10¹⁰ metric tons of cellulose, making this simple polymer one of the most abundant compounds in the biosphere.

Cellulose compared to starch is much more crystalline to amorphous transition when heated beyond 60-70°C in water (as in cooking).

Cellulose requires a temperature of 320°C and pressure of 25 mpa to become amorphous in water. Many properties of cellulose depend on its chain length or degree of polymerization; the number of glucose units that make up one polymer molecule.

Cellulose from wood pulp has typical chain lengths between 300 and 1700 units, cotton and other plant fibers as well as bacterial cellulose have chain lengths ranging from 800 to 10,000 units.

2.7 CLASSIFICATION OF CELLULOSE

A plant's cell wall is composed of several chemicals, of which cellulose (made up of molecules of the sugar glucose) is the most important. Cellulose molecules are into fibrils which form the structural framework of the wall. The synthetic material called celluloid, as its name implies, was derived from natural cellulose (from cotton and wood) for example; when cellulose is treated with nitric acid, a derivative called cellulose nitrate is formed. An American inventor, John Wesley Hyatt (1837-1920) found a way to soften cellulose nitrate by treating it with ethyl alcohol and camphor. The softened material could be molded into smooth, hard bills, thus, Hyatt brought the game of billiards within the economic reach of more people and saved a few elephants.

Cellulose is then classified to many material;

- Cellulose Nitrate
- Cellulose Acetate
- Cellulose Acetate Butyrate

- Ethyl Cellulose
- Methyl Cellulose
- Carboxyl Methyl Cellulose

CELLULOSE NITRATE

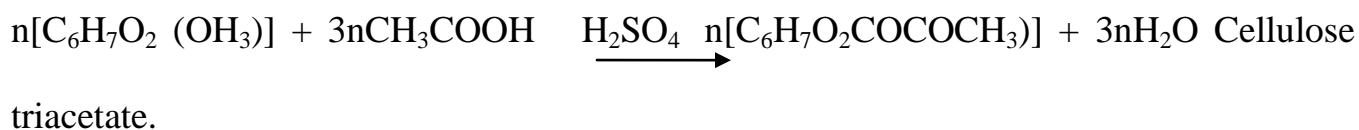
This is known as Nitro-cellulose. It is prepared by reacting cellulose with nitric acid in presence of sulfuric acid which acts as a dehydrating agent. The partially nitrated cellulose mixed with camphor gives the so-called celluloid, which can be easily softened and moulded. The function of camphor is to act as a plasticizer to enhance the moulding properties. $n[\text{C}_6\text{H}_{10}\text{O}_5]$

Cellulose nitrate is also used as smokeless gunpowder. Celluloid was removed from the market when safer substitutes became available. Cellulose nitrate plastics are transparent, strong and tough. The specific gravity is 1.35 - 1.40. Its dimensional stability is poor as it slowly shrinks due to slow loss of plasticizer and hence is not used for precision parts. It is inflammable. It is resistant to water but is attacked by strong acids and alkalis. It tends to discolor with age. It becomes brittle at low temperature.

Nitro cellulose containing 10.5 - 11.5% N is used for moulded extruded articles, that explosive gun-cotton. Cellulose nitrate plastics are used for tool handles, spectacle frames, drawing instruments, pens, toothbrush handles, table tennis balls, radio dials, picture films and many fanly articles. The first “artificial leather” was made by centrys fabric with nitro cellulose suitably covered and embossed, which is still used in coverings following blocks, laggage and upholstery.

CELLULOSE ACETATE

This is white, odorless, tasteless, non-toxic solid. It is manufactured having substitution ranging from 2.3-3.0 or from 53 to 62.5% combined acetic acid. Cellulose acetate is obtained by treating cellulose with concentrated acetic acid or acetic anhydride in presence of a catalyst such as H_2SO_4 .



The resulting cellulose bioacetate is partially hydrolyzed to render it soluble in organic solvents such as acetone. It has good clarity, stability toughness, impact strength and resistance to UV radiation. It has a high dielectric strength, high tensile strength and resistance to mineral acids. It has good film and plastic strength. It is used for preparing fibers for textiles on one hand and for preparing transparent sheets on the other.

CELLULOSE ACETATE BUTYRATE

It is a copolymer having lower water absorption than the cellulose acetate alone. It is prepared by treating cellulose with a mixture of acetic acid and butyric acid in presence of H_2SO_4 (catalyst). Its thermal stability and other properties are similar to that of cellulose acetate plastics but has better chemical and moisture stability, better dimensional stability and impact strength. It is used for toothbrush handles, combs, buttons, pens, automobile hardware.

ETHYL CELLULOSE

Ethyl cellulose is prepared by treating cellulose first with caustic soda to produce the caustic cellulose and then allowing it to react with ethyl chloride to give an average of 2.0 ethyl groups per $\frac{1}{2}$ ethyl cellulose monomer. Ethyl cellulose is the toughest of all cellulose plastic. Chisel handles, mallet heads and light, it has good chemical resistance and stable to heat and light, it has good electrical properties and hence films, foils, and sheets and made from it are used for electrical insulation purposes. Special compositions have been used to produce rain coat surgical tapes, laminated glass sheets and straw like

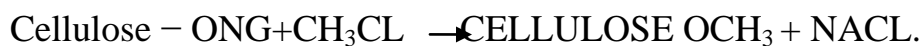
extrusions for weaving furniture seats. Its toughness and flexibility are retained through wide range of temperature, it has excellent solubility in many cheap solvents and hence foils and films with good strength and toughness can be prepared by casting its solutions.

Ethyl cellulose is obtained by the replacement of hydrogen atoms by ethyl groups in the reactive hydroxyl groupings in cellulose. It is not necessary to complete the reaction as in the case of cellulose acetate.

Ethyl cellulose plastics are made by mixing ethyl cellulose with plasticisers and other ingredients either an open rolls in an internal mixer such as Banbomy mixer. Ethyl acetate moulding powders have widely been used for pressure and extrusion purposes.

METHYL CELLULOSE

Methyl cellulose can similarly be prepared from alkalis cellulose by treating with methyl chloride.



CARBOXY METHYL CELLULOSE.

Carboxy methyl cellulose is prepared as its sodium salt, by the reaction of cellulose with NaOH (Sodium Hydroxide) and chloroacetic acid, it has been used as a thickening agent in textile additives, cosmetics, cakes, ice cream e.t.c. it has also been used as a protective colloid in suspension and emulsion polymerization system.



Generally, cellulose occurs in plant life, cotton or wood cannot be shaped, moulded, cast or extruded, for performing these processes, it is necessary to modify it. Cellulose can be modified in the following manner.

Regenerated cellulose:

- Cellulose is brought into the solution form, it is the temporary modified form of cellulose from this modified form fibres. Or films are shaped by spinning or casting and then regenerated to the original cellulose chain forming rayon or cellophane. When cellulose is brought into a solution by means of a chemical reaction and it is reprecipitated out of the solution to give essentially the same

chemical structure in the form of film or fibre. It is said to be regenerated cellulose. In this transformation of shape, there is not much change in chemical and physical properties of cellulose. ieces and allowed to age under controlled conditions of temperature and humidity. During ageing, the high polymer molecule breaks down a little. The breakdown is indicated by better solubility in solvents.

- Rayon – rayon is the name given to fibres (filaments cut into small lengths) and continuous yarns made of regenerated cellulose. Rayon is also made by a method similar to that used in the manufacture of cellophane. The only difference is that the viscose solution is extruded through spinnerets into the acid bath instead of extruding it through a narrow slot into the acid bath. Thus, a major part of rayon and cellophane are derived from the easily hydrolysed xanthate of cellulose. When the xanthate is extruded in solution into a bath of dilute acid as a sheet or thin stream. It is rapidly hydrolyzed, regenerating a slightly degraded form of cellulose as a sheet (cellophane) or as fibre (rayon).

Under cellulose acetate the following are manufacture of cellulose acetate:

Pretreatment of cellulose- pure cellulose is dried at about 50°C to a moisture content of less than 4%. It is then pretreated with small amount mineral acids in order to increase the reactivity of cellulose to break it down to make it more soluble.

Reaction with acetic anhydride-100 parts of dry pretreated cellulose are mixed with a mixture of 200 parts of glacial acetic, 100 parts of concentrated H_2SO_4 . The temperature is maintained between 10^0c after 2hrs, the mixture first become fluid and then start thickening up. When cotton fit in remains, the process gets completed of the process generally takes about 5hrs.

2.8 HERMICELLOSE

Hemi cellulose is a polysaccharide related to cellulose that comprises ca. 20% of the biomass of most plants. In contrast to cellulose, hemi cellulose is derived from several sugars in addition, especially xylose but also including mannose, galatos, rhamnose and arabinose. Hemi cellulose consist of shorter chains, around 200 sugar units. Furthermore, hemi cellulose is branched, whereas cellulose is unbranched.

2.9 BREAK DOWN (CELLULOLYSIS)

Cellulolysis is the process of breaking down cellulose into smaller polysaccharides called cellodextrins or completely into glucose units, this is a hydrolysis reaction.

Because cellulose molecules bind strongly to each other, cellulolysis is relatively difficult compared to the breakdown of other polysaccharides.

Most mammals have only very limited ability to digest dietary fibres such as cellulose. Some ruminants like cows and sheep contain certain symbiotic anaerobic bacteria (like cellulomonas) in the flora of the rumen, and these bacteria produce enzymes called cellulases that help the micro-organism to breakdown cellulose, the breakdown products are then used by the bacteria for proliferation. The bacterial mass is later digested by the ruminant in its digestive system (stomach and small intestine).

2.10 FUNCTIONALITY

Cellulose has many uses as an anticake agent, thickner, and getting agent but these are generally subsidiary to its most important use of holding onto water.

Water cannot penetrate crystalline cellulose but dry amorphous cellulose absorbs water becoming soft and flexible. Some of this water is non-freezing but most is simply trapped. Less water is bound by direct hydrogen bonding if the cellulose has high Crystallinity, but some fibrous cellulose products can hold onto considerable water in pores and its typically straw-like cavities, water holding ability correlating well with amorphous (surface area effect) and void fraction (that is, the porosity). As such water is super coolable, this effect may protect against ice damage. Cellulose can give improved

volume and texture particularly as a fat replacer in sauces and dressings but its insolubility means that all products will be cloudy.

Cellulose can also be said to function as follows:

- It is rigid and so gives structural support, shape and form to the cell.
- It protects the protoplasm of the cell.
- It is also permeable of water, gases e.t.c.

2.11 USES OF SUGAR

Sugar is used in variety of forms water, gases etc.

The most common is granulated sugar which is used by many people to sweeten hot drinks and breakfast cereals. Sugar can also be bought in cubes, which are made by pressing wet sugar into mould before drying. Icing sugar, used to coat cakes and pastries, is made by grinding the sugar crystals into a fine powder.

Other sugars include caster sugar finer than granulated and used for jams and jellies and brown sugar (for color and flavor). Syrups and treacle (for spreading) are liquid forms of sugar.

Sugar is not first a sweetener, it can be used in a number of different ways:

- As a preservative –at the right concentration sugar helps to stop micro – organisms growing and so prevents food spoilage in jams and other preserves, it helps to produce subtle changes in flavor.
- Sugar softens the acidity and sourness in foods such as mayonnaise, tomato products and tart fruits such as gooseberries and grapefruit.
- sugar gives the characteristic texture to a variety of foods
- from jams to ice cream and cakes as a bulking agent.
- To raise the boiling point or lower the freezing point which can be essential in some recipes, e.g making ice cream.
- To speed up the process of fermentation (by yeast) in baking which makes the dough rise, e.g in bread and tea cakes.
- It makes cakes light and open – textured when it is beaten with butter or eggs.

Sugar in Foods.

Sugar is added to many foods for flavor, texture, color and safety. By reading the ingredients panel on food packaging labels you can see how many ordinary foods contain

sugars. Remember glucose, fructose, sucrose and lactose. (milk sugar) are all sugars.

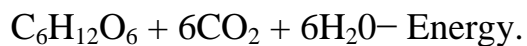
Other names from sugars include dextrose, invert sugar and maltose.

Other uses of sugar include.

- It is use in healing of wounds.
- It is use by chemical manufacturers to grow penicillin.
- It can be added to concrete to acid the setting process.
- It absorbs moisture and therefore keep your biscuits crunchy?
- It helps flowers stay fresher for longer when added to the water.
- It makes the 'glass' used in film stunts.
- It is also used in production of ethanol.

2.12 FUNCTIONS OF SUGAR

Glucose is used in respiration to provide energy for the activities of plants and animals and is also stored in the muscles and live in the form of glycogen.



- Glucose is used to build up proteins or fats. These proteins are used for growth and for the building up of materials for new cell walls such as cellulose.

- Sugar, either the pentose, ribose, or its 2- deoxy-derivative, both in the furanose form are structural components of nucleic acid. Deoxyribonucleic acid (DNA) present in the nucleus of cells is the genetic material, and indirectly controls the synthesis of proteins.

2.13 PROPERTIES OF CELLULOSE.

Cellulose has no taste, it is odorless, it is hydrophilic with the contact angle of 20 -30. It is insoluble in water and most organic solvents, is chiral and is biodegradable. It can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature.

Many properties of cellulose depend on its chain length or degree of polymerization. The number of glucose unit that make up one polymer molecule.

Cellulose is soluble in cupriethylenediamine (CEO), cadmium ethylenediamine (cadoxen), N-methylmorpholine, N-oxide and lithium chloride/dimethylformamide. This is used in the production of regenerated celluloses (as viscose and cellophane) from dissolving pulp.

2.14 METHODS OF PRODUCING GLUCOSE FROM CELLULOSE

Glucose is obtained from paper making sludge by first removing calcium carbonate from the sludge to produce a mixture substantially depleted of calcium and containing cellulose.

Using the methods of Acid Hydrolysis, we tend to produce Glucose.

Acid Hydrolysis (Hydrochloric Acid): Substitute 5% sulfuric acid with 5% hydrochloric acid and repeat the same procedures as in sulfuric acid.

Procedures: For both hydrochloric acid and sulfuric acid.

- Prepare 5% sulfuric acid and 5% of hydrochloric acid.
- Weigh out the grams required using the weighing machine
- Pour into a 1000ml volumetric flask.
- Add water to make up the mark and Shake vigorously until it mixes together.
- Then you allow it to settle down before usage.

3.0 CHAPTER THREE

METHODOLOGY

In order to achieve or obtain the objective of this project “kinetic study of hydrolysis of cellulose (saw-dust) using hydrochloric acid” some certain laboratory work was carried out. Therefore this chapter will base on the equipment/apparatus used and the procedures involved in the experimentation.

3.1 MATERIALS AND EQUIPMENT

3.1.1 Materials: saw-dust (cellulose) used in the production of glucose production was collected from timber shade, New G.R.A, Trans-Ekulu Abakpa Nike Enugu.

APPARATUS:

- 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

3.1.3 Reagent

- Sulphuric acid (5%) solution
- Hydrochloric acid (5%) solution
- Potassium hydroxide (5%) solution
- Distilled water
- Cellulose source (wood chips, carboxy-methyl cellulose,
- Glucose solution
- Benedict's solution

3.2.1 Hydrolysis (Acid hydrolysis)

Aim: The aim of this process is to convert cellulose to simple sugar by the method of hydrolysis.

Theory: The earliest method of hydrolysis of cellulose to sugar is by ethanol and water hydrolysis but acid hydrolysis was used in this experiment. The starting material was saw-dust which was obtained from the woods. Acid hydrolysis can be achieved using different acids in which two acids and one base was used at constant temperature (80%).

We used two acids: Sulphuric acid (H_2SO_4) and Hydrochloric acid (HCL).

Method 1 and 2 are as follows:

Procedures:

10g of saw-dust was weighed and mixed with 100ml of distilled water; it was poured into a beaker and was stirred thoroughly. Then it was put into a heating mantle for one hour at a constant temperature of $80^{\circ}C$ before adding the required amount of sulfuric acid and hydrochloric acid into the sample. The sample was heated again for another one hour, and was repeated for like five (5x) e.g 10g, 20g, 30g, 40g, 50g. The sample was filtered out with a filter paper, the acidity of the sample was checked using universal PH, when the color is orange it is acidic, then we add the potassium hydroxide (KOH) to make the sample neutral or colorless.

3.2.3 Colorimetric Analysis of Glucose (using Benedict's solution)

Aim: To use a colorimetric analysis method and a calibration graph to identify the percentage of glucose in the unknown solutions.

Theory: The commonest method of analyzing sugar in hydrolyzed cellulose is by using an instrument called calorimeter, Fehling's solution test, front titration test Trinder glucose activity test but Benedict's solution was used. It was achieved by measuring the Benedict solution in each sample in equal proportion.

Procedure:

0.1, 0.2, 0.3, 0.4, 0.5 grams of standard glucose solution was weighed (stocked solution) and dissolved in a small beaker with distilled water, it was poured into 50ml volumetric flask and was filled up with distilled water to make up the mark.

5ml from the two unknowns (H_2SO_4), (HCL) and standard glucose concentration each was measured into test tubes, 10ml of Benedict's solution was added to each of the concentration. The test tubes were placed into a water bath at constant temperature of 95°C for five (5) minutes, then it was removed and placed into a beaker of cold water to cool and settle for another five (5) minutes. After that the solutions was poured into a cuvette, before placing them into a visible spectrophotometer at constant wavelength of (610) to find the absorbance readings.

The unknown glucose concentrations was determined using **BEER LAMBART LAW**.

The beer lambart law (or beer's law) is the linear relationship between absorbance and concentration of an absorbing species.

The formula is stated below :

$$A = ELC$$

Where A = Adsorption

E(epsilon) = Adsorptivity of solution

L = Wave length

C = Concentration

This obtained data will enable you to draw a glucose concentration calibration graph, which could be used to identify the glucose percentage in each of the unknown solutions.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Results

This chapter contains the results and discussion of sugar content in each concentration of acids (HCl and H₂SO₄) at constant temperature. The tables below shows the results obtained from glucose analysis and glucose yield with HCl, and H₂SO₄, 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.

TABLE 4.1**Variation of Absorbance with the standard Glucose Concentration.**

STANDARD GLUCOSE CONCENTRATION (g)	ABSORBANCE
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(H₂SO₄)	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

DISCUSSION

The results obtained in the various experiments with different acids conducted under this research project could be well interpreted to discuss the effects of various acids on cellulose conversion to glucose.

The rate of hydrolysis is greatly influenced by acids and this affect the glucose yield produced (fig 4.1). Increase in concentration of acids like HCl or H₂SO₄ enhances the hydrolysis process positively, as the cellulose hydrolyzed more with increase in concentration of acid.

However, for standard glucose concentration, it was observed that the optimal yield of H₂SO₄ and HCl (0.940) and (1.280) respectively.

From the experiment conducted on the acid hydrolysis, it was noticed that H₂SO₄ hydrolyses faster, followed by HCl. It means that H₂SO₄ and HCl took time in breaking the glucosidic bond of cellulose, converting it to sugar.

The results obtained on glucose concentration analysis showed that HCl has relatively higher absorbance (1.280) yield at 1.244g, followed by H₂SO₄ yield (0.940) at 0.887g.

From the graph plotted (standard glucose concentration against each concentration of acid), It can be seen that the standard glucose concentration was drawn containing the absorbance values of the two acids given.

For the sulphuric acid:

The optimum absorbance is 0.887g. They are indicated here using blue dotted line which shows us the glucose concentrations.

For Hydrochloric acid:

The optimum absorbance concentration is 1.244g, they are indicated also using black dotted lines.

In terms of HCl, increase in concentration result in increase in glucose yield.

This shows that further research will result in getting to equilibrium curve, the higher the glucose concentrations, the higher the absorbance.

From the table 4.1, it is evident that the optimum concentration for standard glucose is 0.05g. This is because after 5 minute of heating, the glucose concentration is required to settle under the test tube, when put into a cold water for another 5 minutes.

In table 4.2, the sulfuric acid absorbance concentration is lower than the other acid; and the optimum values of both HCl and H₂SO₄ is 50ml respectively.

In table 4.3, it was observed that the hydrochloric acid absorbance concentration is higher than the other acid.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATION.

5.1 CONCLUSION

This research project has shown the possibility of using cellulose (saw-dust) for industrial sugar production through acid hydrolysis.

The yield of glucose from hydrolyzed cellulose is affected by various acids, which includes; HCl and H₂SO₄. It was observed that the highest yield of glucose was obtained at the optimum glucose and is at 1.280% for HCl. Thus, it is evident that the concentration of absorbance increases with an increase in the glucose concentration at a limited (fixed) wavelength (610). Therefore, the best acid hydrolysis is hydrochloric acid.

As the concentration of glucose increases, the yield of absorbance equally increases up to inhibit the standard glucose concentration which causes a decrease in the absorbance yield.

Finally, production of sugar from local raw material such as cellulose (saw-dust) by acid hydrolysis could be considered viable economically.

5.2 RECOMMENDATION

Having carefully and keenly taken part in the research work and taken note of various yields of glucose from these two acids (HCl and H₂SO₄).

The following recommendations were made by the researcher based on the results of the study:

- I recommend that the HCl acid should be used in order to get the highest yield that will result to the equilibrium curve.
- The application of the acid hydrolysis of cellulose should be employed in large scale sugar manufacturing in Nigeria as this will provide another means of producing sugar and also will save the country a great deal of foreign exchange.
- The use of commercial or processed saw-dust (cellulose) is more profitable and less expensive, also much faster and easier than extraction of cellulose from rice husks.
- This study is strongly made for the government, investors, industrialists and other business individuals with the capital to invest into this new method of glucose hydrolysis- acid hydrolysis. This will help to increase the availability of cellulose in the market, provide employment, reduce the cost of sugar in the country, and improve the exportation of glucose from Nigeria, thereby, making our economy an industrialized economy.

References

- Adas Micheal J.E. and Ollis, D.F.1986, *Biochemical Engineering Fundamentals*, 2nd Ed., p163-172, McGraw-Hill,
- Austin, G.T (1914), *Shreve's Chemical Process Industries* (5th ed,) McGraw Hill, United State Pp 554-670.
- Bailey, J.E, and Oilis, D.F (1986). *Biochemical Engineering Fundamentals*, 2nd ed, Chapt 3, McGraw Hill.pp 110-150
- Bradbury J.H (2006). *Simple Wetting Method to Reduce Cyanogens content ,* " *Journal of Food Composition and Analysis* (Elsevier, New york) (4ed.) pp 388-398.
- Brown, W.H and Poon, T.(2005), *Introduction to Organic Chemistry* (3rd ed), Wiley ISBN 0-47144451-0. Pp 550-650
- Bertran, M.S. and Dale, B.E, 1985. *Enzymatic hydrolysis and recrystallization behavior of initially amorphous cellulose*, *Biotech. Bioeng.*, **27**, 177,
- Eliasson A.N (2004). *Starch in Food Structure, Function, and Applications* Wood Head Publishing. ISBN 9780849325557.

Greenwood, N.N and Earnshaw, A (1997). *Chemistry of the Elements (2nd ed) Oxford: Heinemann, ISBN 0080379419 pp 384.*

Ghose, T.K., 1977, Cellulase biosynthesis and hydrolysis of cellulosic substances, in *Advances in Biochemical Engineering, 6, 25, pp 345*

Grethlein, H.E. 1985 , Comparison of the economics of acid and enzymatic hydrolysis of newsprint, *Biotech. Bioeng, 20, 503, 1978. Erickson, L.E., Energetic efficiency of biomass and product formation, Biotech. Bioeng, pp21, 725.*

J Mendham, Denney RC, Barnes JD, Thomas MJK (2002), *Vogel's textbook of quantitative chemical Analysis (6th ed) pp 508*

Linko M.1977, an evaluation of enzymatic hydrolysis of cellulosic materials, in *Advances in Biochemical Engineering, 5, 39.*

Lubert S; Berg, J M; Tymoczko, J I, (2002), *Biochemistry (5th ed.) San Francisco: W.H. Freeman. ISBN 0-7167-3051-0.*

Smith, A.M (2001), The Biosynthesis of Starch Granules. *Biomacromolecules (2nd ed).*
No 2. Pp 335-41

Yudkin J, and Hough L, (2002). *Sugar Chemical, Biological and Nutritional Aspects of sucrose.* Butterworth. ISBN 0-408-71072-2.

APPENDIX I**The conversion of glucose concentration in percentage to glucose concentration in grams.**

For the standard glucose concentration (5ml);

I. 50ml contains 0.1g of glucose = 0.2%

5ml will contain =?

$$5/50 \times 0.1\text{g} = 0.01\text{g}.$$

$$1/10 \times 0.1 = 0.01\text{g}$$

II 50ml contains 0.2g of glucose = 0.4%

5ml will contain =?

$$5/50 \times 0.2\text{g} = 0.02\text{g}$$

$$1/10 \times 0.2\text{g} = 0.02\text{g}$$

III 50ml contains 0.3g of glucose = 0.6%

5ml will contain =?

$$5/50 \times 0.3\text{g} = 0.03\text{g}$$

$$1/10 \times 0.3\text{g} = 0.03\text{g}$$

IV 50ml contains 0.4g of glucose = 0.8%

5ml will contain =?

5ml will contain =?

$$5/50 \times 0.4\text{g} = 0.04\text{g}$$

$$1/10 \times 0.4\text{g} = 0.04\text{g}$$

V 50ml contains 0.5g of glucose = 1.0%

5ml will contain =?

$$5/50 \times 0.5\text{g} = 0.05$$

$$1/10 \times 0.5\text{g} = 0.05\text{g}.$$

APPENDIX II

The conversion of glucose concentration of the acids in grams to percentage (%) yield calculations.

For sulphuric acid:

$$1 \quad 0.025/10 \times 100 = 0.250$$

$$0.0025 \times 100 = 0.250\%$$

$$2 \quad 0.042/10 \times 100 = 0.420$$

$$0.0042 \times 100 = 0.420\%$$

$$2 \quad 0.059/10 \times 100 = 0.590$$

$$0.0059 \times 100 = 0.590\%$$

$$3 \quad 0.079/10 \times 100 = 0.790$$

$$0.0079 \times 100 = 0.790\%$$

$$4 \quad 0.094/10 \times 100 = 0.940$$

$$0.0094 \times 100 = 0.940\%$$

For Hydrochloric acid:

$$1 \quad 0.024/10 \times 100 = 0.240$$

$$0.0024 \times 100 = 0.240\%$$

$$2 \quad 0.052/10 \times 100 = 0.520$$

$$0.0052 \times 100 = 0.520\%$$

$$3 \quad 0.076/10 \times 100 = 0.760$$

$$0.0076 \times 100 = 0.760\%$$

$$4 \quad 0.105/10 \times 100 = 1.050$$

$$0.0105 \times 100 = 1.050\%$$

$$5 \quad 0.128/10 \times 100 = 1.280$$

$$0.0128 \times 100 = 1.280\%$$

LIST OF TABLES

Table 4.1: Variation of Absorbance with the standard Glucose concentration.

Table 4.2: Variation of Absorbance with Sulphuric acid

Table 4.3: Variation of Absorbance with Hydrochloric acid

LIST OF FIGURE

Figure 4.1: Graph of Absorbance of the acid against the glucose concentration.