Introduction

INTRODUCTION

Cellulose is one of the oldest natural polymers. It is renewable, biodegradable, and can be derivatized to yield various useful products. It is fabricated by many plants as hairs (cotton) or as a structural polymer in cells. It is also produced enzymatically by bacteria (bacterial cellulose). Its main source, however, is wood, a natural composite, where cellulose is contained in combination with lignin in a texture which certainly represents a masterpiece of natural architecture. This natural polymer composite must be destroyed for isolation of cellulose (pulping).

Cellulose and wood are most abundant in nature; they are produced in a sustainable way and offer many possibilities for use. Its assets are that it is renewable, biodegradable, biocompatible and derivatizable. It is possible to base a whole chemistry on cellulose, which, however, today can't compete with petrochemistry on the grounds of costs. Several disadvantages of cellulose include its expensive production, its sensibility to water, and its slow regeneration- a tree must have at least 30 years before it can be used for   cellulose production.

The pulping and bleaching stages are two important stages involved in the complex process of converting fibrous raw material into paper. Papyrus was the first material used for writing, as early as 3000 BC in Egypt. Paper has been used in China since a century before Christ, when raw materials were rags and plant tissues. The consumption of paper has steadily increased by about 2.5 % every year since the beginning of the last century (1) and paper is by far the most widely used carrier of information in that time. In order to make paper out of lignocellulosic materials e.g. woods and straws,

the fibers have to be liberated. In principle, this is done in two ways, either mechanically or chemically.

Main Components of Lignocellulosic Materials :

The main components of Lignocellulosic materials such as wood or agricultural residues, consist of three dominating polymers; cellulose, hemicelluloses and Iignin.

Cellulose:

Cellulose is a linear homopolysaccharide composed of 3-D-glucopyranose units which are held together by only one type of linkage , namely (1, 4) - glycosidic bonds.

Cellulose is the most abundant natural polymer in the world. It is estimated that 830 million tons of cellulose are produced each year through photosynthesis [2]. It is a colorless macromolecule having the formula $(C_6H_{10}O_5)_n$, a polymer of anhydro-D-glucose units. Cellulose molecules may contain up to 7000- 15000 anhydro-D-glucose units in a single chain [3]. Cellulose molecules are hygroscopic, this is the reason that water has such an affinity for cellulose, due to that each unit contains 3-OH groups. The cellulose formula is shown as follows:
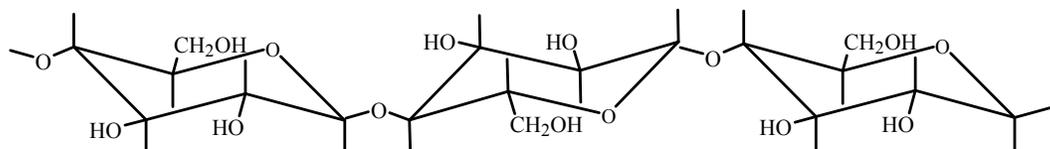

Stereo-Chemical Formula of Cellulose

Hemicellulose:

Hemicellulose is similar to cellulose in many ways. It is a colorless polymer of sugar, forms hydrogen bonds, has great affinity for waters and has a similar elemental composition. However, hemicellulose is not as uniform as cellulose; also the degree of polymerization (D.P.) of hemicelluloses is much less than that of cellulose. According to (Gram 1983)[4] hemicelluloses occur mainly in the primary wall and their degree of polymerization in sisal fibers lies between 50 and 200. Hemicellulose is heterogeneous polysaccharides, it is made up of several six- carbon sugars: glucose, mannose and galactose, and five- carbon sugars: xylose and substitute groups such as acetyl groups and uronic acid. On the other hand cellulose chains are strictly linear.
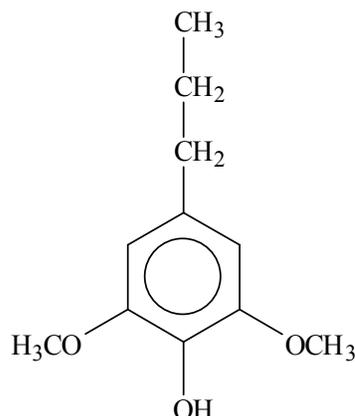
Lignin:

Lignin is amorphous, highly complex, mainly aromatic polymer of phenyl-propane units joined by benzilic and phonetic ether linkages and c-c linkages. The DP of lignin is only in the order of several hundreds. The mechanical properties reflect broadly their composition with a high stiffness and strength associated with a high level of cellulose [5]. It can be classified in several ways but they are usually divided according to their structural elements [6]. All plant lignins consist mainly of three basic building blocks of guaiacyl, syringyl and p-hydroxyphenyl moieties, although other aromatic type units also exist in many different types of plants.
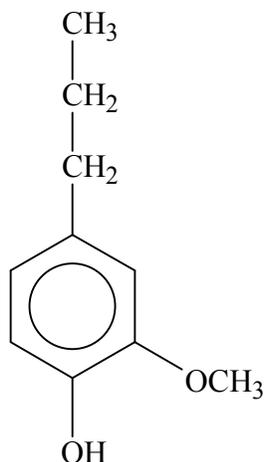
Guaiacyl propane

(Hardwood & Softwood)

Syringyl propane

(Hardwood)

Lignin Building Blocks

Lignin constitutes 20-30 % of the dry matter in wood, in softwoods, the average lignin content is approximately 28 % and in hardwood is about 23 %. The lignin macromolecule is a random, three dimensional structure with no crystalline regions [7]. Lignin is colored ranging form off-white as in wood, to dark brown as Kraft cardboard boxes or paper bags. The formula of lignin is $C_9H_{8.83}O_{2.3}$–$(OCH_3)_{0.96}$. The function of lignin in plants is an encrusting agent in the cellulose/hemicelluloses matrix. It is often referred to as the plant cell wall adhesive. Both lignin and extractives in plants reduce the digestibility of grasses in animals. Lignin is also associated with the hemicellulose forming, in some cases, lignin-carbohydrate complexes that are resistant to hydrolysis even under pulping conditions.

Minor Components:

Extractives are those components in wood, which can be dissolved (extracted) in ethanol, toluene, benzene or other neutral solvents or mixture

of solvents. The extractives are made up of: volatiles, resin acid, fatty acids and finally a neutral fraction of alcohols, phenols….etc.

Ash:

Ash is defined as the residue after complete combustion of paper at 925 ± 25 ^{o}C, which consist of mineral matter in pulp [8].

Local Lignocellulosic Raw Materials:

Since there are no wood plants in Egypt, other residual plants can be used to produce pulps. Lignocellulosic fibers such as bagasse, cotton stalks, cornstalks, rice straw, jut, sisal, flax….etc, have had some application in different composites [9]:

Bagasse;

Bagasse is the solid Lignocellulosic residue left after extracting juice from the sugar cane stalk. In some countries; the principal use of bagasse is as a combustible material for energy supply in sugar cane factories in thermal power station, but in many other countries such as Egypt, Cuba, and Brazil … etc. It is used in pulp and paper industries and for fiberboard materials [10]. Together with molasses, bagasse is a by-product (grayish-yellow residue) from the sugarcane industry, which grows extensively in tropical countries [11,12].

Some bagasse is burned to supply heat for the sugar refining operation; some is returned to the fields; and some finds its way into various board products. It is composed of fiber and pith [11]. The fiber is thick walled and relatively long (1-4 mm). For use in composites, only the fibrous portion

is utilized. Atchinson and Lengel (1985) [13] reported the history and growth of bagasse fiberboard and particleboard at the 19th Washington state particle board Symposium.

The chemical composition of bagasse is remarkably consistent among different geographic sources, is made up of cellulose (40 %), hemicelluloses (30 %), lignin (15 %) and a balance of hot water extractable materials and amorphous pith. As mentioned, only the bagasse fiber is utilized for the production of the highest quality composition panels.

Cereal Straw:

After bagasse, cereal straw is probably the second most important agricultural fiber for composite panel production. Cereal straw include straw form wheat, rye, oats and rice. Straw like bagasse is an agricultural residue. Unlike bagasse, large quantities are generally not available at one location. Straws have high ash content and they tend to fill up fireboxes in boilers and increase the wear rate on cutting tools. Their high silica content tends to make them naturally fire resistant.

Plants have existed in several countries to make thick (5-15 cm) straw panels with Kraft paper faces [14]. The low density of these panels makes them fairly resilient, and test data show that housing built using these panels is especially earthquake resistant. Straw can be used to supplement part of the fiber content in wood particle board. A large particle board plant substituted straw at a rate of 8 % and found no major problems except that the sander dust from the faces deposited additional ash in the boiler. This plant then stopped using straw in the face and used it only in the core.

Introdcution

At a rate of 10 % or less, the effect on the tool wear was not significant [15]. For the production of fiber-based products, straw can be pulped using alkali treatments and refining. Ray grass straw particleboard was commercially produced in USA [16].

Rice Straw:

Rice straw is the main Lignocellulosic material in Egypt and is used to produce fiberboard. Most rice straw is inferior in quality to that made of wood fiber as a result of the high percentages of non-fibrous materials included in straw. When care is taken to fiberize the rice straw, boards properties increased significantly [17].

However, the material is heavy and difficult to handle, cut and fasten rice straw has been evaluated for its mechanical properties in straw-clay composites [18]. While the produced material was a good insulator, it was not waterproof. Rice straw has also been used to bind clay in built-up walls as well as manufacture of brick for firing. Firing of straw-clay composites results in biomass loss, which can result in a lighter weight product and improved insulation properties [19].

Cotton Stalks:

Cotton is cultivated primarily for textile fibers, and little use is made of the cotton plant stalks. Stalk harvest yields tend to be low and storage can be a problem. The cotton stalk is plagued with parasites to winter over for next year's crop. Attempted commercialization of cotton stalk particleboard was unsuccessful for this reason. With respect to structure and dimensions, cotton stalk fiber is similar to common species of hardwood fiber [20].

Corn Stalks:

Corn stalks, like many other agricultural fiber sources, consist of a pithy core with an outer layer of long fibers. Currently in the US, corn stalks are chopped and used for age, left on the field, or baled for animal feeding. The cobs are occasionally used for fuel; corn stalk and cobs can be made into a reasonably good particleboard and fiberboard [21].

Flax, Hemp, Jute and Kenaf:

These plants are characterized by a high proportion of long, flexible best fibers that are readily separated and purified from the other materials in the plant. Consequently, such fibers have long been used for textiles and rope making. Most of this fiber reaching the paper industry in the past has been secondary or waste fiber. It has been highly prized because of the strength and durability. Flax is grown expressly for high-grade cigarette paper. Kenaf fibers represent 20-25 % of the dry weight of the plant with the pith removed [22]; Kenaf and other fibers have been blended together to make non-woven textile mats.

Other Fiber Sources:

Other important fiber sources include, bamboo, papyrus, sheaves and reed stalks, bamboo is an important source of raw material for fiberboard in tropical countries. Most varieties of bamboo are fast growing and produce strong fibers particleboard. Coutts (1997)[23] illustrated those fibers from naturally accruing plants can provide the building blocks for a wide range of materials that can compete on a "performance for cost" basis with these more advanced materials.

The disposal of lignocellulosic wastes is a major environmental problem. Using them in construction could reduce the magnitude of the problem. However, there are several issues that are limiting their exploitation such as their compatibility with cement, toxicity and limited strength [24]. Construction is a material intensive activity and consumes large amounts of materials. Therefore, the utilization of such wastes in making cement-bonded construction materials offers an attractive to their disposal.

Conventional Pulping Processes:

The pulp industry had its beginning in the middle of the last century when the rising tide of literacy and increasing demand for fiber to use in paper. The conventional pulping methods had been designed on the basis of the utilized technique, mechanically or chemically. The chemical pulping processes had been classified principally as alkaline or acidic pulping processes.

Mechanical Pulping:

The mechanical pulping process could be produced from holding a wetted stick against a grindstone. The defibering action in mechanical pulping resulted from a loosening of fiber by repeated compression-decompression cycles to which the water plasticize fibers are subjected by the travel of the alternating high and low profile of the abrader removing at right angles to the fiber axis [25,26].

Chemical Pulping:

(i) Alkaline Pulping:

It is based on the use of a reagent that will react with lignin in the wood in a manner that will result in its dissolution. Caustic soda has been used for this purpose for more than 100 years. However, the pulp showed strength properties superior to those of any pulp known at that time was named "Kraft Pulp". The term Kraft pulping has evolved to summarize all the processes involving heating of wood chips in an aqueous solution of sodium hydroxide and sodium sulfide from approximately 70 ^{o}C to a cooking temperature of about 170 ^{o}C, then sustained for 1-2 hours cooking period [27-29].

(ii) Sulfite Pulping:

The sulfite processes are based on the fact that lignin will react with sulfurous acid, bisulphite, and neutral sulfite, either alone or in combination, and that the produced lignin sulfonates can be extracted from wood [30]. Whereas entirely new pulping processes have supplemented the original mechanical, alkaline and acidic processes developed in the last century, important technical changes have and are occurring. In each of these processes new generation pulp and/or processing techniques were developed. In mechanical pulping, the development of techniques for the economic bleaching of such pulps is an important goal. The efficient modem alkaline pulp mill has evolved as a result of development of improved recovery methods. In sulfite process, new generation pulps, magnetite and multistage magnetite allow greater strength than that produced by calcium base.

Introdcution

The research has been developed towards sulphur and chlorine-free chemical pulp production. The goals which should be achieved are:

- The method developed must be capable of using all the main fibrous raw materials.
- It must be possible to produce fully bleached paper-grade pulp without sulphur or chlorine chemicals.
- Sulphur and chlorine must not be replaced by elements such as nitrogen that could pose new risks to the environment.
- The yield and paper making properties of the pulp must be reasonably good.

Bleaching Processes :

Bleaching is the destruction or solubilization of coloring materials to make it possible to wash out the color substance or the alteration of coloring materials to cause it to reflect white light more truly. Practically, a commercial bleaching process must preserve or further develop the chemical or physical properties of the stock and is frequently expected to achieve a definite degree of pulp purification. This can be done by removal of some constituents of the unbleached pulp and modification the remainder. The operations applied depend entirely on the character of the unbleached pulp and the quality desired of the bleached pulp. Bleaching materials may be divided into two general classes, namely, oxidizers and reducers. Any active oxidizing agent, hypochlorites, chlorites, elemental chlorine, chlorine dioxide, ozone, peroxides and others can be used for the pulp bleaching. Sulfur dioxide or other sulfur compounds such as sodium sulfite and calcium bisulphite are examples of reducing agents which have the opposite effect, in action on pulp, of oxidizing agents. Brightness property is

a very important sales point. The bleaching plants today are designed for even higher brightness.

The conventional methods of bleaching always use chlorine or one of its components to bleach pulps. Due to environmental aspects, this chemical (chlorine) can`t be used today; therefore oxygen or one of its components (oxidizing material) is used to bleach pulp in non-conventional bleaching methods.

Oxygen-based chemicals for pulp bleaching

The current attention being directed to the elimination of chlorine compounds in pulp mill bleaching. It is believed that conventional bleaching is a chief contributor to toxicity which is detectable in the pulp mill effluents.

Reducing pollution from bleaching pulp mills had been the driving force in developing new bleaching processes, by using friendly environmentally bleaching chemicals.

The use of oxygen-based chemicals such as oxygen, hydrogen peroxide and per acids had exhibited a dramatic growth during the last several years. In this context, the primary advantage of using oxygen-based bleaching includes the following reasons:

1) Replacement of chlorine-based chemicals (especially chlorine gas or for elementally chlorine-free pulp production). Consequently eliminations of all chlorine-based chemicals in totally chlorine-free sequences is recommended

2) Energy saving, oxygen productions require 1/8 of the energy equivalent amount for chlorine.

(i) Oxygen bleaching practices and benefits:

Oxygen bleaching was developed as a commercially feasible process during the late sixties and early seventies in Sweden and South Africa. The main process obstacle until that time was that all oxygen treated pulps were degraded and thus had poor strength properties. In 1968, a group in France discovered that certain magnesium compounds, when incorporated in an oxygen stage, reduced the cellulose degradation [31].

(ii)Oxidation of Lignin by Molecular Oxygen:

Autoxidation of phenolic and enolic units in alkaline media is an example of initial attack on activated positions by a radical species. During bleaching using molecular oxygen in alkaline media, other oxygen-containing species is created which cooperates with oxygen in the degradation process. Autoxidation of phenolic and enolic structure in lignin, enolic structures in lignin and carbohydrates produces hydroperoxy intermediates from which the hydroperoxy anion can be displaced by hydroxide anion in an SN^2 reaction [32, 33].

(iii) Using hydrogen peroxide in pulp bleaching:

Hydrogen peroxide has considerable potential for commercial use in delignification of the unbleached pulp e.g. Kraft pulps prior to the final bleaching in either non-chlorine or conventional sequences [34,35]. In its present state, the technology can not complete with that already developed for using oxygen for the same purpose. The main reason is the high cost of hydrogen peroxide relative to that of oxygen. On the other hand, hydrogen peroxide has not been extensively studied as oxygen. In addition to that, the sensitivity of the course of its reactions to the presence of trace amounts of

transition metal ions and their complexes. Hydrogen peroxide has unparalleled ability to bright the mechanical pulp and other high yield pulps[36]. Research on the hydrogen peroxide oxidation of lignin model compounds had been carried out [37]. Hydrogen peroxide is used in separate bleaching steps, either as lignin-retaining bleaching reagent in the production of high-yield pulps or during a later stage of conventional bleaching sequences. Hydro-peroxide anions add readily to quinonoid and other enone structures, affording hydro peroxide and subsequently oxirane intermediates[38]. Alkaline and / or oxidative degradation of the latter two types of intermediates yield again mainly carboxylic acids, as end products. Hence, the reaction mode of hydro peroxide anions bears strong resemblance to that of hypochlorite.

(iv) Utilization of peroxyacetic acid in the chemical pulp bleaching:

The use of peroxyacetic acid is considered to be a promising method for pre-bleaching of chemical pulps. Peracetic acid is effective and selective in reactions with lignin and it does not possess high reactivity towards carbohydrates [39]. Consequently, both hardwood and softwood pulps with low kappa numbers and high degree of polymerization can be obtained. The residual lignins produced from pre-treatment by using peracetic acid appear to be much more reactive towards alkaline peroxide bleaching [40, 41].

(v) Potential using for Peroxymonosulphate in Bleaching:

Liebergott et al found that dilute aqueous solutions of peroxymonosulphate anion, under mild acidic conditions at low temperature (20 °C – 50 °C) were very effective in delignification of wood [42]. The peroxymonosulphate treatment must be followed by alkaline extraction to

solubilize and remove the fragments of depolymerized lignin. Peroxymonosulphuric acid can be easily produced by mixing a concentrated solution of hydrogen peroxide and sulphuric acid according to the following equation:

$$H_2SO_4 + H_2O_2 \longrightarrow H_2SO_5 + H_2O$$
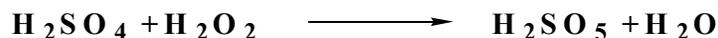
Several experiments were performed to determine the conditions needed to produce significant quantities of peroxymonosulphuric acid [43-44]. It was found that the yield of peroxymonosulphuric acid is greatly dependent on the molar ratio H_2SO_4 : H_2O_2. The more concentrated hydrogen peroxide and the higher mole-to-mole ratio of acid to peroxide increased the yield of peroxymonosulphuric acid.

(vi) Alkali treatment of cellulose:

The path from cellulose I to cellulose II goes by Na-cellulose I. If a cellulose sample is treated with alkali solution, the cellulose swells to various extents depending not only on the type and the concentration of the alkali, but also on temperature. This process means a couplet de-crystallization of the cellulose and the degree of swelling determines the degree of lattice transformation. The most couplet transformation of cellulose I to cellulose II is reached with sodium hydroxide, while other alkalis produce only a partial transformation or non at all [45]. Alkali treatment and particularly treatment with sodium hydroxide causes not only a widening up of the lattice but also a change in the conformation and a shift of the lattice planes. After the removal of surplus sodium hydroxide a new lattice, that of sodium Cellulose I, can be found. In this lattice relatively

large distances occur between the cellulose molecules; the interspaces contain water molecules. It should be noticed that in this case the OH-groups of the cellulose molecules are transformed to -ONa- groups and therefore the dimensions of the cellulose molecule are enlarged.

According to Hayashi et al [46], two forms of Na-cellulose I exist which are obtained by different temperatures from cellulose I. both differ only slightly in the dimensions of the space unit. Na-cellulose I_I can be re-transformed to cellulose I, whereas Na-cellulose I_{II} can only be transformed to cellulose II from which it also can derive. During an intensive washing the linked Na-ions are removed and another lattice is formed, the lattice of cellulose II apart from a change in the dimensions of the space unit the planes of the cellulose molecules are aligned approximately in the 101 direction

Further polymorph forms are cellulose III and cellulose IV, both obtainable from cellulose I as well as from cellulose II. The treatment of cellulose I and II with liquid ammonia results in ammonia cellulose from which ammonia can be removed by evaporation and / or heating. The two modifications remaining after this procedure differ only slightly in their space unit dimensions, but the treatment with water transforms cellulose III_I only to cellulose I, and cellulose III_{II} only to cellulose II. Cellulose IV is obtained from cellulose III as well as from cellulose I and II by high temperature treatment (more 200 ^{o}C in glycerol). There are also two slight differing modifications, cellulose IV_I and IV_{II}.

(vii) Effect of presence of salts during alkali treatment of cellulose:

During alkali treatment of cellulose, some salts are usually used to protect cellulose from being hardly affected by the alkali. One of the most important salts is zinc chloride which can dissolve alone in water if sufficient concentration is used. Zinc chloride is a Lewis acid which is a substance that acts as an electron pair acceptor. So, Lewis base is a substance that acts as an electron pair donor. We donate a Lewis acid by A and Lewis base by :B, often omitting any other lone pair that may be present. The fundamental reaction of Lewis acids and bases is the formation of a complex, A-B, in which A and :B bond together by sharing the electron pair supplied by the base.

The presence of $ZnCl_2$ or other Lewis acids during bisulphite cooking increases the cooking rate of soft and hard wood [47]. Also treatment of wood pulp with sulphuric acid and aluminum sulphate improves aging properties of the resulting fiber board [48]. The addition of 5 % $AlCl_3$, sodium aluminate or aluminum sulphate to the unbleached stack, followed by short-time convection drying at 120 ^{o}C then heating at 150-200 ^{o}C for 1-10 minutes increased the wet strength of bag paper, this increase was affected by heat treatment temperature and time [49]. The use of sodium aluminate and aluminum sulphate improves semichemical pulp to give boxboard with improved physicomechanical properties and superior bunting strength, also when the beating rate of the pulp is increased [50]. Treatment of bleached aspen kraft pulp with 2 % aluminum sulphate and small amount (0.02 %) of cationic polyacrylamide increased kaolin retention to above 85 % [51]. Cellulose was completely hydrolyzed to monosaccharide using dilute HCl in presence of $CaCl_2$ [52].

Thermal degradation of cellulose in organic solvent in the presence of HCl or Lewis acids ($TiCl_4$, $SnCl_4$, $SbCl_5$, $BF_3.Et_2o$) for 5-15 minutes at 100 ^oC resulted in low molecular weight cellulose with increased crystallinity. Degradation in the presence of Lewis acid involved primarily coordination of the acid with the oxygen atom of cellulose [53]. Catalytic thermal degradation of pander cotton cellulose in ethanol in the presence of Lewis acids e.g. HCl, $TiCl_4$ ….etc. resulted in 15-100 fold increase in the specific surface area. Also a significance increase in internal surface area of powdered cotton cellulose was observed after thermal degradation at 100 ^0C in the presence of $TiCl_4$ [54].

The activity of Lewis acids as catalysts of cellulose degradation in the acetylating medium decreased in the order $SbCl_5$ < $SnCl_4$ < $AlBr_3$ < $BF_3.OEt_2$ [55]. Also it was found that pretreatment of birch chips with $MgCl_2$ solution (up to 5 %) prior to soda cooking had positive effects on pulp yield and quality, 3-5 % increase in pulp yield was found due to $MgCl_2$ pretreatment, no further increase in yield was found on using more than 5 % $MgCl_2$ [56].

Paper Making:

The significant pulp properties from the paper making stand point are:

- The fiber morphology
- The amount and distribution of the chemical constituents of the pulp fibers.
- The shape, size distribution and physical condition of the pulp fibers.

The first two properties depend on the raw material as well as the type of the pulping process used. The physical condition of the pulp fibers also depends upon these factors, but the third is determined by the fiber preparation or fiber treatment process.

Beating:

Cellulose fibers must be subjected to mechanical treatment (beating) before manufacturing paper. Paper made from unbeaten stock has low strength, porous and unfit for most uses. Well-beaten fibers can be readily formed into a uniform sheet paper of quite high density. In general, beating improves some properties of fibers and contrary has bad effects on others. Increased beating within the commercial range improves tensile strength but generally tends to decrease tear resistance.

Paper sheet formation:

The term sheet formation is used in reference to a property of paper (degree of fiber dispersion) and also in reference to the act of forming the wet fiber into paper. The elements of formation are degree of fiber dispersion, extent and type of fiber orientation, and degree of packing or solid fraction. In order to obtain uniform fiber dispersion for the paper machine, the stock must be screened until it becomes free of fiber clumps, or lums, dirt and other foreign matter.

Paper sheet Properties:

The type of fiber used, the extent of pulping bleaching, and the degrees of bending between fibers determine, to a large degree, the physical and optical properties of the paper as follows:

(i) Tensile strength:

It is a measure of the resistance of paper to the direct tension. It is a force required to break a strip of paper which has a specified length and width of 15mm. In tensile strength measure in paper industry is not true because we measure the breaking load per unit of width rather than per unit area. Thus, we use the term breaking length, which is equal to:

$$\text{Breaking length (m)} = \frac{\text{Tensile strength x 66700}}{\text{Basis weight}}$$

Paper will break under reduced load; the time of load application is increased. Length of the strip affects the tensile strength (specific length is 180 ± 1.0 mm).

Tensile strength is always greater in machine direction than that in the cross direction. Increased weight of paper increases the tensile strength. Tensile strength is important in the new sprint and other paper prints where high tensile strength is an important property.

(ii) Burst strength:

It is the hydrostatic pressure required to rapture the paper when deformed in an approximate sphere 1.2 inch in diameter. A controlled rate of loading pressure transmitted to paper rubber diphram through an annular clamp holding sheet against orifice. Pressure at the time of rapture is recorded on a synthetive. Increasing of the loading rate tends to increase the reading because it increases the tensile strength which is a component of bursting strength. Burst strength is a complex function of the tensile strength and stretch.

(iii) Tear Resistance

Tear resistance is measured on a pendulum type instrument which measures the amount of work done in tearing paper through fixed distance after tear has been started by mean of a cutter attached to the instrument. Work done in tearing is measured by the difference in the potential energy of the pendulum at the beginning and the end of swing since pendulum is swinging to right angle equal to the initial displacement. Dividing the work done in tearing paper by the distance torn give average tearing force required to tear paper. Tear factor is measured by dividing the tear strength in gram by the basis weight in gm/m^2. Tearing resistance is directly related to the fiber treatment.

(iv) Optical Properties:

The optical properties of paper, such as brightness and opacity, are important like physical properties of paper. Some important factors affecting the optical properties of the paper sheet are:

- Degree of whiteness of the pulp,

- Presence of dyestuff or colored pigments,

- Method of stock preparation and sheet formation, and

- Presence of minor ingredients (e.g. rosin and starch).

Aging and Accelerated Aging:

Depending upon natural and environmental conditions, paper is subject to attack from several sources. Heat, sunlight, moisture and dust are the main agents which cause deterioration in its properties. Paper in storage deteriorates with time, even under perfect conditions. This change, which takes the form of yellowing and subsequent embrittlement, is known as

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natural aging. The roles of acidic groups and carboxyl groups particular, which are important factors for yellowing, had been studied by various investigators [57-60]. Deterioration increases with increase of temperature and exposure, for even short periods, to high temperatures which causes paper to become yellow and brittle. Low temperatures however retard the process of aging. The extent of this deterioration, which leads to changes in chemical, mechanical and optical properties of paper [61 -66], depends on the type of fibers [67, 68]. Many authors [69-73] had concerned with the structural changes of cellulosic materials under accelerated heat aging. Accelerated aging is the only suitable method to study the effects of different aging parameters on paper properties, since natural aging takes place on a prolonged time. Some authors correlate aging and accelerated aging; they showed that accelerated aging at 100 ^{o}C of 72 hrs equivalent to 25 years of natural aging [74].

During the aging of papers, the ce1lulosic components of the fiber walls sustain alterations which result in an extensive drop of strength properties. Many investigations were concerned with the effect of accelerated heat aging on papers made from pure cellulose fiber and bleached chemical pulps of various origins [75-77]. Other investigations were made on the permanency and durability of letterpress printing papers [78], books and documents [79] and maps [80]. Permanency refers to the extent which a paper will retain its original properties upon storage. The extent to which a paper is permanent is generally measured by the loss of original strength as indicated by fold and tear tests. Durability refers to the extent to which a paper will resist deterioration when subjected to handling. Some papers are permanent as filter papers, sanitary tissues and other papers made of pure cellulose. Durable papers are those made for shipping bags, tags,

cartons and wrapping purposes. Bond and ledger papers, also index bristols are both permanent and durable, and are used for court and legal records, library index cards etc., where papers must not only last a long time but also must withstand the deteriorating influence of frequent use or handling.

The dry aging has been used by many, and much data from it has been published [81, 83]. The simplicity of this method and the experience accumulated with it make it attractive. The moisture content of the aged paper largely affects the results obtained. To carry out moist aging, either the samples are conditioned to the desired moisture content in sealed tubes or accelerated aging chambers with air containing the proper moisture content may be used. Limited oxygen supply and retention of the degradation product would have caused sealed-tube aging results to be different [84, 85]. Opinions vary as to the causes and importance of paper destructions [79, 86-88]. Preservation of books [89, 90] and components of library materials [91] take a great attention due to its vital importance. Acidity formed in book papers due to prolonged exposure to storage conditions (temperature, humidity, dust and microorganisms) was removed by morpholine vapor and water vapors [92].

The changes in properties brought about by ultraviolet (U.V.) irradiation, heat exposure and by a combination of both treatments were determined [93]. The validity of accelerating aging tests to predict and rank papers on their permanence had been under question, preventing the development of performance-based standards for permanent paper. They conducted a general kinetic analysis to investigate the aging process of

paper. A general model was proposed to describe the depolymerization of cellulose [94].

A critical review was given for the degradation of the cellulose in the low-temperature region (below about 300 $^\circ$C) of the power transformer operation [95]. The large number of kinetic studies, under a variety of environmental conditions from kraft paper in insulating oil, to cotton and paper in oxygen, were considered in terms of a first-order polymer chain scission model. In many cases, the data were replotted to suit the model. Common activation energy of 111$\pm$ 6 kjmol^{-1} was calculated where it was shown that the pre-exponential factor, rather than the activation energy, is sensitive to the oxidizing nature of environment and susceptibility to degradation of the material. The chemical mechanisms of degradation were reviewed, and conclusions and recommendations were made regarding chemical condition monitoring and life prediction of electrical insulation.

Paper is a complex structure of composite biological fibers. The behavior of paper is time-dependent with respect to load, moisture content, or temperature, whether these control parameters are fixed or varied in combination. A key question is whether the time-dependent properties are a consequence microstructure, thinner fiber bond, the fiber distribution in a sheet, or combination of them. For each type of loading and ambient control variation, the possible physical mechanisms inducing the observed response, the mathematical models proposed as tools for the design of both the paper-making process and applications [96].

Accelerated aging of wood kraft insulating paper by means of a pulsed KrF excimer laser radiation on the degradation of wood kraft paper in

air was systematically investigated [97]. During the laser irradiation experiments, the temperature of the paper samples was real-time measured by means of an IR camera. It is shown that the ageing temperature of the paper can be controlled very precisely by simply adjusting the laser parameters. Indeed, leveling-off temperatures in the $25 - 320$ ^{o}C range can be reached after only 3 seconds of laser exposure, by either varying the repetition rate at a fixed energy density or changing the laser flounce at a given pulse rate. By performing both scanning electron microscopy (SEM) observations and measurements of the degree of polymerization (DP) of the laser irradiated paper samples, it was able to demonstrate that the laser irradiation induced a very rapid degradation of the paper samples (typical laser exposure times are around 35 seconds to be compared with ~10 days for standard dynamic heating based ageing tests).

Both the D.P. of the irradiated paper samples and the average width of the corresponding cellulose fibers as measured from SEM micrographs, were reduced by about 50 % following their laser heating at ~320 ^{o}C for 35 seconds of exposure time. It was pointed out that the observed laser-induced degradation is predominantly a photothermal process. Finally, by using gas chromatography/mass spectrometry (GC/MS), it was able to show that low molecular weight compounds such as acetaldehyde, methyl format, acetone, and methanol were produced not only by the laser ageing process but also in real on-field transformers underwent a severe short-circuit.

A link was drawn between paper hornification and low temperature thermally-accelerated ageing of paper based on a review of existing research[98]. Similarities between treatment temperature, humidity, resultant physical properties, and possible degradation mechanisms were enumerated.

Hornification can be explained by irreversible intra-fiber hydrogen bonding, whereas accelerated ageing is normally attributed to chain scission and cross linking. However, in the light of the similar experimental protocols used to investigate each, the possibility of both mechanisms occurring in both experiments was considered. The short time scales of hornification would seem to preclude chain scission and cross linking, but it seemed possible that irreversible hydrogen bonding occurs during dry accelerated ageing.

The thermal stability of paper-making pulps under conditions of accelerated aging and at pyrolytic temperatures was examined. Degradation was found to be extremely complex and influenced by both the technical processes of paper-making and by the experimental methods used. At moderate temperatures, as used for accelerated aging, the folding endurance test was found to be a sensitive measure of degradation. Methods of reducing the variability of the test were considered, and a new technique capable of handling widely different results was developed and evaluated.

Several paper-making pulps were artificially aged and the resultant loss of strength attributed to the interaction between a gradual fiber strength reduction and a rapid increase in interfiber bonding. Excessive initial inter-fiber bonding decreased hand sheet stability. Softwood sulfite and kraft pulps were more stable than a birch kraft pulp, but the behavior of sulfite pulps varied greatly. The presence of Iignin or high hemicellulose content was not of itself sufficient to cause rapid aging.

The pyrolytic behavior of pulps was investigated using thermo-gravimetric analysis. Paper-making pulps had mean pyrolytic activation

energies between 30-45 kcal/mole. The activation energy decreased as the reaction proceeded. Correlation of these activation energies with the rate of loss of physical properties during accelerated aging was not good. The results indicated that the rate determining reactions for pyrolysis and for low temperature degradation are different but that the pyrolytic behavior is partially determined by the supramolecular structure. Empirical stability indices, based on both the integral and differential thermograms, were calculated, and these correlated well with the relative rates of loss of physical properties [99].

Molecular characteristics of cellulose during accelerated aging were studied over wide temperature and time ranges. Also mechanical properties of model samples of paper made of cotton, sulfate, and sulfite cellulose were studied. Interrelation of the molecular characteristics of cellulose and strength properties of paper was investigated [100].

Aim of the work:

The aim of this work is to study the effect of alkali treatment of cellulose paper pulp in presence of zinc chloride at different concentrations on its aging properties. This aims to produce document papers which can be stand for a longer time than the untreated samples. To study this effect, we caryout complete analysis for the physical properties (strength properties, optical properties) and chemical properties also crystallinity by X-ray, scanning electron microscope (SEM) and IR spectroscopy for the samples treated with different alkali concentrations. The used pulp in this work is a high α-cellulose bleached wood pulp.