3. INTRODUCTION

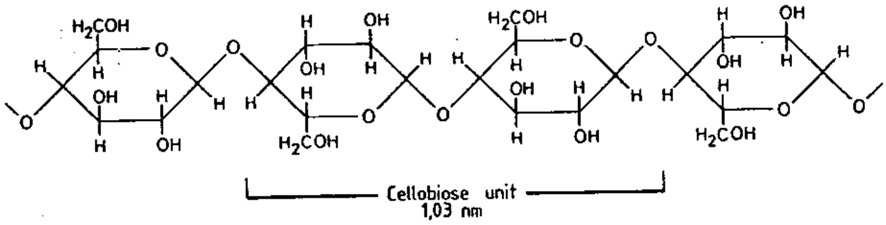
3.1. Lignocellulosic Materials and Their Chemical Composition

Natural wood and artificial boards represent the most important sources for construction purposes, building of houses, furniture, packaging, boat building, transport vehicles, and many other spheres. Both wood and agricultural residues are organic materials formed during the growth of plants by the subdivision and elongation of cells.

Lignocellulosic materials (wood and agricultural wastes) are complex polymeric structure consisting mainly of lignin and carbohydrate. Also present, but not contributing to lignocellulosic material, are minor amounts of other organic chemicals and minerals. The organic chemicals are diversed and can be removed from the lignocellulosic materials with various chemical agents or solvents. The minerals constitute the ash residue remaining after ignition at a high temperature. The chemical components of the lignocellulosic materials can be described in details, as follows:

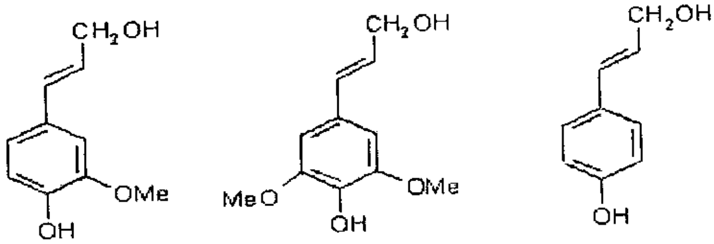
3.1.1. Cellulose

Cellulose is a linear organic polymer of empirical formula $(C_6H_6O_5)_n$, where n represents the degree of polymerization. Cellulose consists basically of anhydroglucose units linked through 1, 4-β-glucosidic bonds. The production of cellulobiose octa-acetate by acetylosis of cellulose provide the first piece of evidence that the monomeric form of cellulose is a cellulobiose molecule consisting of two glucose units linked together through 1, 4-β-glucosidic linkage. This proposal is now generally accepted so that cellulose may be regarded as long chain polymer composed of cellulobiose monomer units where n represents the degree of polymerization. Glucose molecule unit contains three hydroxyl groups, a primary alcoholic hydroxyl group in position C-6 and two secondary hydroxyl groups at position C-2 and C-3. These alcoholic groups undergo typical chemical reaction characteristic of primary and secondary alcohols and are responsible for the hydrophilic nature of cellulose (1, 2).



3.1.2. Lignin

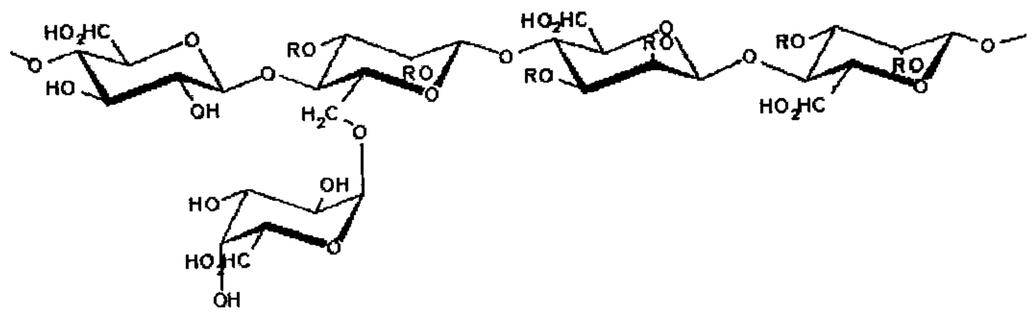
Lignin is the non-carbohydrate fraction of extractive free wood and forms the adhesive reinforcing component which binds the cellulosic fibers structure. Lignin is probably the most complex, difficult to characterize natural product (3). It does not occur alone in nature and is impossible to remove from the wood structure in high yield without considerable degradation. Lignin is an amorphous polymer insoluble in water but soluble in sodium hydroxide or sulfite solution and many organic solvent (4). Lignin is essentially substituted phenyl propane three dimensional polymers in which the phenyl propane units are held together by ether and carbon-carbon linkage. The presence of phenolic and alcoholic hydroxyl groups contributes to its polar nature and to formation of hydrogen bonds (5) On the basis of the number of methoxy groups attached to aromatic ring, the phenyl propane units are divided into *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units. The proposed structural scheme of lignin building units was shown in the following figure (6).



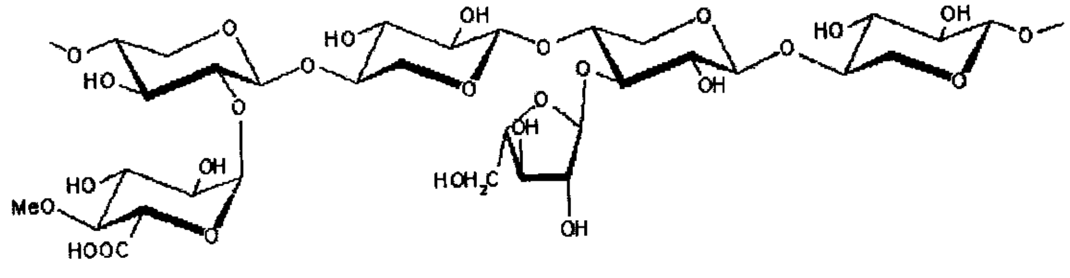
Coniferyl alcohol Sinapyl alcohol para-Coumaryl alcohol

3.1.3. Hemicelluloses

Hemicelluloses are low molecular weight heteropolysaccharide when compared with cellulose. Hemicelluloses are soluble in aqueous alkali and often in boiling water (4) which consist of following monomers; D-glucose, D-mannose, D-galactose, D-xylose, L-arabinose, L-rhamnose, D-glucuronic acid, 4-O-methyl-D-glucuronic acid and D-galacturonic acid. Hemicelluloses are therefore heterogeneous in their chemical constituents and non-crystalline (5). Although cellulose and hemicelluloses are chemically bonded; the extensive hydrogen bonding and the physical intermixing of both structures make quantitative separation of the two compounds impossible. On the other hand, the existence of chemical bonding between lignin and hemicelluloses is evidenced (7). The main hemicelluloses in softwoods are galactoglucomannans but also arabinoglucuronoxylans, arabinogalactans and some other polysaccharides are present.



Structure of galactoglucomannans.



Structure of arabinoglucuronoxylans.

Hardwood and agricultural lignocelluloses hemicelluloses consist of glucuronoxylans, glucomannans and some other polysaccharides. The major component of hardwood hemicelluloses is an O-acetyl-4-O-methyl glucurono-β-D-xylan, also known as glucuronoxylan.

3.1.4. Extractives and mineral matters

The extractive materials are those substances which are soluble in water and organic solvents such as benzene, ether, alcoholic-benzene mixture…ect. Extractives include materials such as oils, resins, wax, tannins, starch, dye stuffs, proteins, gums, and organic acids. The extractives contribute to wood properties such as color, odor, and decay resistance.

Most mineral matters present in the plant materials are held in strongly adsorbed form or combined with organic or inorganic matters are insoluble form. Calcium, potassium, magnesium, silicon, iron, aluminum, manganese, and sodium usually make up of the metallic elements present in the plant (7).

3.2. Lignocellulosic Composite Board Types.

3.2.1. Particle board

Particleboard is defined as a panel product manufactured from lignocellulosic materials, combined with a synthetic resin or other suitable binder and bonded together under heat and pressure. The primary difference between particleboard and other reconstituted wood products, such as waferboard, oreinted strandboard, medium density fiberboard, and hardboard, is the material or particles used in its production. The major types of particles used to manufacture particleboard include wood shavings, flakes, wafers, chips, sawdust, strands, silvers, and wood wool. The term particleboard sometimes is used generally to include waferboard and oriented strandboard, which are manufactured primarily with wood flakes and wafers. Particleboard pertains only to panels manufactured from a mixture of wood particles or otherwise from wood particles other than wafers and flakes. Particleboard manufacturing falls under Standard Industrial Classification (SIC) Code 2493, reconstituted wood products, which include hardboard, insulation board, medium density fiberboard, waferboard and oriented strandboard in addition to particleboard (8, 9).

3.2.1.1. General steps of particleboard preparation

i-Preparation of raw material

In case of non-wood raw material, lignocellulosic agricultural wastes (agro-based fibers) are delivered to the mills usually in bale form. After removal of building wire, bales are spilt by hand before passing the material to the cutters. The length of the cut chaff must be uniform as possible (15-50 mm) and the powdered chaff dust as well as metallic foreign substances must be eliminated by magnetic separator (10). The raw material used in our study was sugar-cane bagasse which is the most abundant agricultural residues available in Egypt; for particleboard manufacturing.

ii- Treatment with additives (adhesives)

Urea-formaldehyde and melamine-formaldehyde adhesives are the commonly bonding agents used for the production of particleboard and medium density fiberboard. The polymerization of these resins takes place by condensation, which is a normal chemical reaction between two active groups. Water is usually evolved as a by-product of this reaction. This type of resins is called thermosetting resin adhesive.

Sizing materials can be also be added to increase the water repellency of the board. The common hydrophobic agent used for particleboard is the paraffin wax, which can be applied as an emulsion into the dilute stock or melted onto the surface of the mat before pressing (10). Emulsion contains 1 % paraffin wax mixed with 10 % urea-or melamine-formaldehyde (both based on dry wet of the lignocellulosic material) was used to prepare binding material for lignocellulosic composites.

iii- Sheet formation

After preparing the raw material, with or without resin it is felted to form the board by dry or air felting process, in which the mat is formed of low moisture content (10 %) (11).

iv-Hot pressing

The press applies heat and pressure to activate the resin and bond the fibers into a solid panel. Although some single-opening presses are used, most domestic particle board platens are equipped with multi-opening batch presses. Total press time is generally 2.5 minutes for single-opening presses and up to 6 minutes for multi-opening presses. Continuous presses may also be used to produce particleboard. Presses generally are heated using steam generated by an onsite boiler that burns wood residue. However, hot oil and hot water also are used to heat the press. The operating temperature for particleboard presses generally ranges from 149 to 182 ^{0}C (300 to 360 ^{0}F.) The presses used to manufacture molded particleboard products are not platen presses, but are press molds equipped with a heated die that shapes the resinated lignocellulosic particles into the finished product. Press temperatures can range from 132 to 288 ^{0}C (270 to 550 ^{0}F.) Press temperature and time vary according to the molded product being produced (8, 9).

v-Conditioning and trimming

After pressing, the boards generally cooled prior to stacking. The particle board are sanded and trimmed to final dimensions, any other finishing operations (include laminate or veneer application) are done, and the finished product is packaged for shipment. The boards withdrawn from the press with a humidity of about 1 % and temperature ranging from 150 to 200 ^{0}C have no moisture balance. As the temperature decreases below 100 ^{0}C, they start to regain humidity from the edges, while no absorption takes place in inner part of the board because of the high temperature and mixing of saturated air. Therefore, the edges of the board expand in length, width, and thickness whereas no change occurs in the part of the board and this leads to the well known wrapping. Wrapping can be prevented if the moisture balance is achieved in special devices where both temperature and relative humidity are adjusted. There are two humidification systems:

A-Discontinuous conditioning system (conditioning chambers). In this chamber, the relative humidity is 80-85%, the temperature is 38-50 ^{0}C and the time required up to 5 or 6 hours (12).

B-Continuous conditioning system is a machine has rollers immersed in water through, which they pick up water, then ejected it into the boards when they pass through the machine (13). In other continuous humidifying system, the water is sprayed by nozzle onto the screen-back board, and vacuum is applied from the other side for sucking excess water. After humidification, boards are trimmed to the required size using longitudinal and cross cutters normally equipped with tungsten carbide tips.

3.2.2. Fiberboards

According to the International Consultation on Plywood and other Wood-based Panel Products (Rome, 1963), believed that the definition established at 1957 consultation in Geneva was outdated and should be a mended as follows (14) "a panel made of fibers of wood or other lignocellulosic material and manufactured by an interfelting of fibers into a mat followed by compacting between rolls or in a platen press". Bonding agents and other materials may be added during production to improve certain features such as mechanical properties and resistance to moisture, fire, insect, and decay". Rome consultation retained the density classification of fiberboard adopted at the Geneva consultation which classify fiberboard by density into two groups:

1- Non-compressed fiberboards,

2- Compressed fiberboards.

These two groups are further subdivided into a total of five density ranges with limits indicated below:

A-Semi-rigid insulation board: with density from 0.02-0.15 gm / cm^3.

B-Rigid insulation board: with density from 0.15 to 0.4 gm / cm^3 in certain parts of the world it is called soft board (15), insulating board (16), structural insulation board (17) and wall board (18).

C-Intermediate or medium density fiberboard: with density from 0.4-0.8 gm /cm^3. It is also called semi-hardboard and low density hardboard.

D-Hardboard: has a higher density from 0.8-1.20 gm /cm^3 and greater rigidity than the previous types. It can be divided into two groups:

-Regular or standard hardboard: with density over 0.8 gm /cm^3 and thickness of 3.2 and 4.8 mm.

-Treated hardboard: after pressing, hardboard can be treated by either heat treatment or oil treatment. It is also called super-hardboard.

E-Special densified hardboard (1.20-1.45 gm /cm^3): pressing the sample at high pressure is required for manufacturing electrical instrument panels.

Medium-density fiberboards were made by the forest products industry (19). Medium density fiberboard (MDF) is one of the many different composite produced from wood particles with various shapes and dimensions that are glued or otherwise bonded together. In addition to wood, also non-wood lignocellulosic materials (agro-fibers) such as straw and bagasse are used in the composite board industry. Typical wood composites are particleboard made from discrete pieces or particles, fiberboard made from defibrated wood, waferboard manufactured from large flakes (wafers), and oriented strandboard made from compressed strands lined up and arranged in layers. The manufacturing processes usually involve combining the wood particles with a synthetic thermosetting resin such as urea-formaldehyde (UF) or phenol formaldehyde (PF) and sizing agent followed by hot pressing during which interparticle bonds are formed.

3.2.2.1. General steps of preparation of fiberboards

The preparation of fiberboard is carried out by the most steps mentioned in particle-board, except that the agro-fibers used in the form of pulp with using wet felting process instead of air or dry felting process.

3.2.2.1.1. Preparation of Pulps

The hardboard pulps can be prepared by different pulping processes which can be divided into chemical (20), semi-chemical (21), and mechanical processes (22). Chemical pulping was divided into four chemical processes of commercial importance (23, 24, 25, 26), namely, the soda sulfite, soda sulfate, soda, and neutral sulfite. Mechanical pulping was divided into three pulping processes, namely, low temperature disc refining (27), high temperature explosive defibration (Masonite process) (28), high temperature disc defibration (Asplund process) (29).

3.3. Lignocellulosic Composites in Egypt

Egypt is one of the countries that have no natural forest (30). Over the last thirty five years and up till now considerations are given to minimize the imported woods and to increase the production of artificial boards made from local agricultural residues (non-wood e.g.; fibrous materials, rice straw, sugar-cane bagasse, flax waste, and cotton stalks). The types of lignocellulosic composites which are already produced from our wood mills are particleboard from bagasse and flax waste, as well as medium density fiberboard (MDF) from bagasse.

In production of local lignocellulosic composites, synthetic formaldehyde-based adhesives, such as urea-formaldehyde, is used in combination with hot pressing in order to obtain boards with good mechanical properties. During the curing of the urea-formaldehyde adhesive in the hot press, some of the free formaldehyde is gassed off into the air causing several environmental and health problems upon exposure to high concentrations (31-33), thus can produce spasms, edema of the larynx, and some studies investigated that formaldehyde is carcinogenic factor. For environmental and economical reasons, it is of interest to produce lignocellulosic composites with low health effects of formaldehyde. This subject is the ultimate objective of this thesis.