CHAPTER-1

INTRODUCTION

Forests have multifunctional role, ecological as well as economic. Forests have a profound effect on all three components (soil, water and air) of biosphere which form the basis of life on earth. Besides, providing environmental services like carbon sequestration, pollution abatement, amelioration of climate, in-situ conservation of biodiversity and maintenance of ecological balance, forests act as the storehouse of innumerable products such as timber, fruits, seeds, gums, resins, medicines etc. Among all the forest products, wood has always been the major forest product since the dawn of human civilization. Though the contribution of forests to mitigation of global warming through sequestration and storage of carbon dioxide has become an international consensus gradually, but that of wood through carbon storage in wood products, substitution of wood products for more energy-intensive materials and reduction of carbon dioxide emission by the use of wood as energy source has not been well recognized yet in the society.

Forests are one of the most valuable resources of earth and vital for existence of mankind. In 2010, the world’s estimated growing stock of wood totaled 527 billion m³ in all forests and plantations and 15 billion m³ in other wooded land. At present total annual wood removal from the forest is 3.4 billion m³. In the past decade alone, about 130 million ha of forests were lost, of which 40 million ha were primary forests (FAO, 2010). The forests loss and degradation was estimated to cost the global economy between USD 2 trillion and 4.5 trillion a year (Sukhdev, 2010).

Forest Survey of India in its recent report on Indian forests (ISFR, 2015) estimated forest and tree cover of India as 79.42 million ha (24.16% of geographical area of country. The estimated annual production of wood from forests is 3.175 million m³ and potential production is 42.77 million m³ per annum from trees outside forests, while annual consumption of wood in household construction, furniture, industrial constructions and agriculture implements is about 48 million m³ (ISFR, 2011). With the requirement of 33% of geographical area under forests as per
guidelines of national policy 1988, the felling from the natural forest has almost seized, whereas increasing population and economic development of country is raising demand of wood and wood products. This demand is fulfilled by import of large quantities of wood from other countries.

1.1 Wood

Wood, an oldest composite material, consists of flexible cellulose fibers assembled in an amorphous matrix of lignin and hemicellulose polymers. These three principle constituents make up cell wall and are responsible for most properties of wood. Technical knowledge and skills have been acquired and applied to harness wood for meeting the needs from time to time. Wood, the predominant source, is among the most extensively used engineering materials. As a consequence, it occupies a position of great importance in the global raw material scenario. Because of ever-increasing demand for wood as well as new restriction on wood production. The need for wood products with enhanced engineering properties and performance is greater than at any time in past. Physical and chemical properties of any wood decide its end utilization. Therefore, the major structural components of wood are discussed which may alter during any preservation process and decay.

1.1.1 Wood microstructure

Wood in the tree trunk is divided into two zones, outer light coloured sapwood, in which the parenchyma cells are alive and metabolically active and inner harder and darker wood known as heartwood in which cells are dead and physiologically inactive. Commercial timbers fall into two main categories-softwoods (obtained from confers i.e. gymnosperms) and hardwoods (obtained from broad-leaved species i.e. angiosperms). The wood structure of gymnosperms is relatively simple and homogenous. The xylem in softwood consists mainly of tracheids and, to a small extent, of parenchyma cells. The latter are generally arranged as uniseriate xylem rays aligned radially in the wood. In addition to ray parenchyma, axially aligned parenchyma cells and resin canals surrounded by epithelial cells also occur in the wood of various genera. The wood of more evolved angiosperms has a more heterogeneous structure consisting of Vessels, fibres, vesicentric tracheids and parenchyma cells.
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The wood cell, which is physiologically dead, is composed of two main parts: cell lumen (which is void space) and cell wall (which is a multilayer structure with interconnecting pits). Cell wall can be sub-divided into Middle lamella (ML), primary wall (P) and compound secondary wall (S). Middle lamella is intercellular space which contains material that holds neighbouring cell elements. It consists largely of amorphous substances like pectin and lignin (matrix). The primary wall is thin layer, consisting of cellulose, hemicelluloses, pectin, and protein and completely embedded in lignin. Secondary wall forms largest layer of the cell wall. It is immediately attached to the compound middle lamella and demarcates cell wall from the cell lumen. Cellulose makes up 94% of the defining chemical substances (Fengel and Wegener, 1984). The secondary wall has prominent layers, usually in the form of an outer (S1), middle (S2), and an inner (S3) secondary wall. (Walker, 2006a).

1.1.2 Wood chemical composition

Rowell (2005) defined wood as a three-dimensional biopolymer composite composed of an interconnected network of cellulose, hemicelluloses and lignin with minor amounts of extractives and inorganics. Cellulose is the main constituent of wood accounting for about 40-50% of dry substance in most wood species, while hemicellulose is 25-40% and lignin is 18-33%. In general, the softwoods have a higher cellulose (40-45%), lignin content (26-34%) and lower pentosan (7-14%) content as compared to hardwoods (cellulose 38-49%, lignin 23-30% and pentosan 19-26%).

Cellulose

Cellulose is present as the main structural component in wood cell walls in the form of microfibrils. Cellulose \((C_6H_{10}O_5)_n\) is a high molecular weight linear chain polymer composed purely of \(\beta\)-D-glucopyranose units linked together by 1-4-glycosidic bonds with degree of polymerisation up to 10,000 monomeric units. Cellulose has a strong tendency to form intra and inter-molecular hydrogen bonds by the hydroxyl groups on the linear cellulose chains, which stiffen the straight chain and promote aggregation into a crystalline structure and give cellulose a multitude of partially crystalline fiber structures and morphologies. Within each microfibril, highly crystalline cellulose is present at centre surrounded by paracrystalline regions of
cellulose. Water can bound by hydrogen bonds to the hydroxyl groups on the surface of microfibril, but it cannot penetrate the crystalline cellulose, since the hygroscopic hydroxyl groups are mutually stabilized by hydrogen bonds within this region (Zimmermann et al., 2004). The molecular structure imparts cellulose with its characteristic properties: hydrophilicity, chirality, degradability, and broad chemical variability initiated by the high donor reactivity of hydroxyl groups.

**Hemicelluloses**

Hemicelluloses are branched polymers with lower degree of polymerisation (50-300) than celluloses and are essentially amorphous in nature. Large deviations between hemicelluloses in softwood and hardwood are recognized. Hemicelluloses are composed of various sugar units, which can be sub-divided into groups such as pentoses, hexoses, hexuronic acids and deoxy-hexoses. Due to heterogeneous and branched nature with many side groups, hemicelluloses form a predominantly amorphous substance with easy accessible OH and other reactive groups. Hemicelluloses are therefore relatively hydrophilic and sensitive to thermal degradation (Shiraishi and Hon, 2001).

**Lignin**

Lignin is three dimensional molecular polymer of phenylpropene units: guaiacyl (G) units from the precursor trans-coniferyl-alcohol, syringyl (S) units from trans-sinapyl-alcohol, and p-hydroxyphenyl (H) units from the precursor trans-p-coumaryl alcohol. The exact composition of lignin varies greatly within species. Gymnospermous lignin consists almost exclusively of guaiacyl monomers, whereas angiospermous lignin consists of approximately equal ratios of guaiacyl and syringyl units (Whetten and Seredoff, 1995). Lignin is completely amorphous with highly cross-linked network. Due to its cross-linked nature, lignin is quite stable and relatively hydrophobic compared to cellulose and hemicelluloses.

**Extractives**

The extraneous components of wood (extractives and ash) are the substances other than cellulose, hemicelluloses and lignin. They do not contribute to the cell wall structure and are mostly soluble in neutral solvents (Pettersen, 1984). Extractives are
the varieties of organic compounds including lipids, waxes, alkaloids, proteins, simple and complex phenolics, simple sugars, pectin, mucilage, gums, resins, terpenes, starches, glycosides, saponins and essential oils (Shiraishi and Hon, 2001). They contribute to wood properties such as colour, odour and decay resistance. Chemically, these are phenolic and polyphenolic compounds like hydroxystilbenes and tannins, hydroxyl-aldehydes and hydroxyl-ketones, tropolones, coumarins, flavonoids, isoflavonoids and neoflavonoids, quinines, xanthones, terpene acids, terpenoid acids and even fatty acids and their esters (Rao, 1982). Phenolic or polyphenolic compounds, including tannins and hydroxystilbenes, tropolones, coumarins and terpenoid acids, are toxic to wood destroying fungi, while the others impart termite resistance to a wide range of timbers. Certain compounds like hydroxystilbenes and 1-citronellic acid, however, possess both anti-fungal and anti-termite properties (Rudman, 1965; Hillis, 1962).

1.1.3 Wood properties

Wood is designed by nature to perform certain specialized functions in trees such as support for crown, sap conduction and storage etc. Wood is formed in a water saturated environment of living tree, and the water in living tree keeps wood elastic and able to withstand environmental strain such as wind loads. It is porous material thereby serving as conducting system. During tree life trunk of the tree is constantly under stress/ load and fibres of the wood are aligned in axial direction in such as way as to withstand such stresses most efficiently. When tree is harvested, physical changes in structure of wood starts. The cellular structure of wood and the physical organization of the cellulose chain within the cell wall affect the physical and mechanical properties of wood, depending on the direction of loading. Wood may be described as an orthotropic material; i.e. it has unique and independent mechanical properties in the directions of three mutually perpendicular axis (longitudinal, radial and tangential) (Niemz, 1993).

Wood water relations

Nearly all the important properties of wood such as physical, mechanical, resistance to deterioration, dimensional stability etc. are affected by amount of water present in wood. Wood from freshly felled tree is fully saturated
with water. Water can be found in the lumen as free water and within the cell wall as bonded water in wood. When the tree is felled the moisture of wood starts decreasing and moisture content at which all liquid water (free water) is removed from the lumen but the cell wall is still fully saturated (with bound water) is known as fibre saturation point (FSP).

Dry wood can absorb water in liquid form, if in contact with it, or as vapour from the surrounding atmosphere if placed in humid atmosphere. The chemical nature of wood substance, particularly that of polysaccharides makes wood hygroscopic or hydrophyllic (Siau, 1984). The hydroxyl groups of hemicellulose and amorphous region of cellulose molecules are responsible for its great affinity to water which has a very strong tendency to form hydrogen bonds. Lignin, on the other hand, possesses comparatively few free hydroxyls and as a result is much less hygroscopic. When wood is placed in an atmospheric condition it will either gain or lose moisture and try to come to equilibrium with it, this moisture content is called as Equilibrium moisture content (EMC) (Skaar, 1972).

**Dimensional instability of wood**

Dimensional change in wood starts only after all free water is removed i.e. wood is at FSP. Loss of moisture from the wood below FSP results in shrinkage and gain of moisture below FSP cause swelling. Thus it can be said that dimensional instability of wood is only below FSP. These dimensional changes are anisotropic in nature i.e. different in axial, radial, and tangential directions. Average values for shrinkage vary for different wood species but are assumed to be approx. 0.4, 4.0 and 8.0%, for longitudinal, radial and tangential directions respectively. Shrinkage in volume is approximately 12%, but large variations are exhibited among wood species (Kollmann and Cote, 1995). The differential shrinkage and swelling in different growth directions are attributed mainly to the cell wall structure. The difference between axial and the two lateral (radial and tangential) directions can be explained on the basis of respective orientation of microfibrils in the layers of the secondary cell wall, but the reasons for the differences between radial and tangential directions are not well understood. In general, the factors that affect shrinkage and swelling are moisture content, density, extractives content and abnormalities in wood structure (Mantanis et al., 1994). Extractives reduce EMC as well as shrinkage and swelling
because they occupy spaces within cell walls that otherwise could be filled with water (Popper et al. 2006). Mechanical stresses (compression or tension) may cause permanent deformation of wood cells, which in turn affects shrinkage and swelling (Skaar, 1972). The main effect of dimensional instability in wood is opening or sealing of joints, changes in cross-sectional shape, warping, checking, casehardening. Thus, the fact that wood shrinks and swells causes a great problem for the utilization of wood.

1.2 Wood durability and biological wood degradation

Wood in the living tree has its own resistance against wide variety of organisms. After tree is cut, wood starts to deteriorate and biological agents are the major cause of wood deterioration. Deterioration can result from fungi (stain and rot), insects (including termites, carpenter ants), marine borers (small molluscs and crustaceans) and bacteria etc. Decay fungi result greatest financial losses among fungi group while termites are the biggest destroyers among insects. These agents of biological deterioration are most active in tropical regions but also develop in temperate and colder regions.

Wood degrading fungi may be classified as decay, stain, or mold fungi depending upon type of degradation they cause. Wood decay fungi are further classified into brown, white and soft rot fungi each possessing own degradation pattern (Zabel and Morrell, 1992).

1.2.1 Stain and mould fungi

Certain lower forms of fungi develop moulds and stains on wood. Stain fungi cause discolourations in wood without much change in texture and strength of material. The most important stain fungi from economic point of view, are blue stain causing fungi in sapwood of various hard and softwoods. The stain fungi primarily invade parenchymatous tissues in sapwood and the discoloration results from the masses of pigmented hyphae in wood cells. Though they cause little damage to prosenchyma cells, several properties in addition to colour, such as toughness and permeability, may be adversely affected. Mould fungi can be broadly classified as being saprophytic organisms that utilize simple sugars and carbohydrates derived from cell
lumens and do not attack cell wall. Moulds are noticed as fuzzy or powdery growth and affect only on aesthetic appearance of the wood.

1.2.2 Decay fungi

Decay fungi are group of fungi that digest moist wood, causing wood rot. Most decay fungi belong to the Basidiomycetes (spore bearing fungi, the basidium), a few are Ascomycetes and Deuteromycetes (fungi imperfecti). Decay fungi attack cell wall contents (cellulose, hemicelluloses and lignin) causing changes continuously in its appearance, physical and mechanical properties. Fungal hyphae of decay fungi are capable of penetration and destruction of cell wall with the help of extracellular enzyme system.

1.2.2.1 Brown rot

Basidiomycetes group of fungi is principle cause of brown rot in wood. Brown rot fungi are mainly associated with gymnosperms (Gilbertson, 1980). These fungi are characterized by their extensive and rapid depolymerisation of cellulose leading to a rapid loss in wood strength at early stages of decay. Brown rot is normally characterized by an excessive removal of cellulose and hemicelluloses and although demethylation of lignin occurs (degree dependant on fungal species) lignin normally persists as a weak amorphous residual skeleton which easily fractures cubically and crumbles into powder on drying. Residual modified lignin in wood exhibits its characteristic colour and consistency (Zabel and Morrell, 1992).

1.2.2.2 White rot

White rots are caused by Basidiomycetes and by certain Ascomycetes. The common feature of all these fungi is that they can degrade lignin as well as cellulose and hemicelluloses. However, the relative rates of degradation of lignin and cellulose vary greatly according to the fungal species and the conditions within the wood. White rot fungi degrade lignin by oxidative processes, which involve phenoloxidases such as laccase, tyrosinase and peroxidase. Within this range of variation, two broad divisions are widely accepted: selective delignification and simultaneous rot (Rayner and Boddy, 1988; Zabel and Morrell, 1992). They degrade cellulose in less drastic
way than brown rot fungi, since their cellulolytic enzymes attack on molecules only from the ends, splitting off glucose or cellobiose units.

1.2.3 Soft rot

The term “soft-rot” refers to specific type of decay caused by a large number of Ascomycetes and Deuteromycetes, which typically produce chains of cavities with conical ends within the S2 cell wall layers of soft and hardwoods exposed to terrestrial and aquatic environments. Economically soft rot attack is of considerable importance since it causes great damage to wooden constructions, especially in ground contact (Schwarze et al., 2000).

1.3 Wood damage by insects

After the tree is felled, a set of ecological succession of insect borer attack starts which depend upon the moisture content of wood. *Ambrosia* and bark beetles of Coleopterus families Platypotidae and Scolytidae are the first to invade and colonize freshly felled green and sappy wood after felling. As the moisture content of wood approach 50%, their activity ceases and attack of flat headed (Bupresidae) and round headed or longicorn (Cerambycidae) borers starts. They attack and destroy bast, sapwood and heartwood causing serious economic losses. When the timber is fully dry, the dry wood longicorn borer, *Stromatium barbatum* (Cerambycidae), powderpost beetles (Bostrychidae and Lycidae) and carpenter bees (Hymenoptera: Xylocopidae) invade the wood. While, powder post beetles is restricted to sapwood rich in carbohydrates, starch and soluble sugars, *Stromatium barbatum* and carpenter bees bore big holes even in the heartwood of seasoned timber (Thakur, 2000).

Wood destroying termites are the members of order Isoptera. These are social insects living in colonies consisting of castes that differ in appearance and functions. There are over 2,000 termite species worldwide. Termites are widespread in tropical and sub-tropical countries. Of the six major families of termites, subterranean termites are most important and major destroyers of wood and wood products. *Heterotermes indicola* is the most important wood damaging subterranean termite species in India. Termites utilize primarily the cellulose component of wood. Termites vary in amounts of water required to establish successful colonies. Dry-wood termites obtain their water needs from the wood and are highly efficient in their uses of water. Damp-
wood and subterranean termites require more water and invade wood that is constantly moist and usually in ground contact. Some termite species construct earthen tunnels that connect wood above ground with soil for water supply and increasing water moisture content. Subterranean termites build their nests in soil and invade wood which is in contact with soil or build earthen tunnels to get access to wood. Mound building termites build large earthen termite mound above ground and grow fungal garden for feeding (Thakur, 2000).

1.4 General introduction about *Pinus radiata* D. Don

The botanical name of the radiata pine is *Pinus radiata* D. Don. It is also known as “Monterey Pine”, “Remarkable Pine” and “Pino Insigne”. Today there are over four million ha plantations of *P. radiata* worldwide with the largest in Chile, New Zealand and Australia making over 90 percent of the world plantation (Mead, 2013).

Radiata pine is fast growing species with an average harvesting age of 26-28 years (Kininmonth and Whitehouse, 1991). The cross-section of the stem generally reveals light or chestnut brown heartwood surrounded by creamy white sapwood. The heartwood formation starts at the age of about 15 years (Walker, 2006b) and in 20-30 year old trees, 80-90% of the volume consists of sapwood. The cross-section of *P. radiata* wood shows growth rings composed of earlywood and latewood. The transition between earlywood and latewood is gradual (Harris, 1991b). Resin canals are also present which contain and transmit resinous materials. In *P. radiata* heartwood resin acids are the main extractives and account for 70-80% of total extractives. However, in sapwood resin acids and fatty acids are found in nearly equal proportion (Walker, 2006b). General chemical composition and characteristics of *Pinus radiata* are shown in Table 1.1.

The mature *P. radiata* wood is of multiple-use. It is easy to saw, peel, pulp or machine and has good nail and screw holding capacity. It is easy to dry, treat, glue and finish. The wood is suitable for a variety of uses including the manufacture of wood based panels, sawn wood, furniture, cabinets, pulp and paper (Bootle, 2005; FITEC, 2007; Harris, 1991a; TRC, 2007).
Table 1.1 Chemical composition and wood properties of Pinus radiata

<table>
<thead>
<tr>
<th>Property</th>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical</td>
<td>Cellulose</td>
<td>40%</td>
</tr>
<tr>
<td></td>
<td>Hemicelluloses</td>
<td>31%</td>
</tr>
<tr>
<td></td>
<td>Lignin</td>
<td>27%</td>
</tr>
<tr>
<td></td>
<td>Extractives</td>
<td>2%</td>
</tr>
<tr>
<td></td>
<td>Ash content</td>
<td>0.2%</td>
</tr>
<tr>
<td>Mechanical</td>
<td>Basic density</td>
<td>400-500(kg/m^3)</td>
</tr>
<tr>
<td></td>
<td>Modulus of Rupture</td>
<td>62-86 MPa</td>
</tr>
<tr>
<td></td>
<td>Modulus of elasticity</td>
<td>7.3-8.36 GPa</td>
</tr>
<tr>
<td></td>
<td>Hardness</td>
<td>2.2-3.6 KN</td>
</tr>
<tr>
<td>Dimensional swelling</td>
<td>Longitudinal</td>
<td>0.2-0.25%</td>
</tr>
<tr>
<td></td>
<td>Radial</td>
<td>2-3.4%</td>
</tr>
<tr>
<td></td>
<td>Tangential</td>
<td>4-7%</td>
</tr>
<tr>
<td></td>
<td>volumetric</td>
<td>6.2-10.4%</td>
</tr>
</tbody>
</table>

Source: (Uprichard, 1991; Bootle, 2005; Cown, 1992; Black, 2005)

Fast growing nature of wood and reduction in harvesting age to below 30 years affects the quality of timber significantly owing to its higher proportion of juvenile wood. This results in poor dimensional stability, low natural durability and stiffness of the wood (Jayawickrama, 2000; Macalister, 1997; Walford, 1991). *P. radiata* sapwood is highly prone to fungal attack and susceptibility to brown rot fungi is higher than white rot (Bamber and Burley, 1983; Butcher and Drysdale, 1991). Untreated heartwood is severely decayed within 5 years of ground contact (Butcher and Drysdale, 1991). As per the Australian Standard (AS5604, 2003), *P. radiata* wood is classified under natural durability class 4 for both in ground or above ground uses, i.e. wood of low durability with an expected life of not more than 7 years. Therefore, untreated *P. radiata* wood is at high risk of biological deterioration over a wide range of conditions.

1.5 Wood preservation

Wood is used extensively in residential construction and other outdoor applications, where it is exposed to the environment and can be colonized and degraded by a range of micro-organisms. To prevent degradation, non-durable wood products used in applications where they are susceptible to bio-deterioration are treated with biocides. Treated wood is sustainable, inexpensive and an effective building material that requires relatively less energy to manufacture.
Prevention of wood against decay has been a concern since Hartig, (1878) showed that fungi are the casual agents of wood decay. The wood protection industry has traditionally relied on only a few first-generation preservatives like creosote, oil-borne pentachlorophenol and the water-borne arsenicals, principally chromated copper arsenate (CCA). The use of traditional wood preservatives is being subjected to increasing environmental, legislative and consumer pressure. Concerns also exist with issues like potential of copper to impact aquatic systems, potential for metal fastener corrosion as well as general concerns over the ultimate disposal of wood treated with inorganic preservatives. The environmental concerns with metals have led some European countries to move towards non-metallic systems for residential applications.

Over the past few decades, there has been substantial global awareness to develop eco-friendly wood preservatives and those, which do not cause any ill effect on the health of mammals (Onuorah, 2000). Efficacious botanical derivatives can provide an alternative to synthetic pesticides and agrochemical companies have started to focus on these alternatives (Addor, 1995). Recently, herbal extracts that are not harmful to the environment, have been found effective natural preservatives (Sen, 2001). Biological efficacy of natural oils has been studied by various workers (Jermer et al., 1993, Sailer et al., 1998, Paajanen et al., 1999, Ritschkoff et al., 1999, Van Acker et al., 1999).

1.6 Chemical composition and biotoxicity of neem seed oil

Neem tree (*Azadirachta indica* A. Juss.) is native to the arid regions of Indian sub-continent. The plant is also adapted to sub-arid and sub-humid regions of tropical and subtropical region. There are about 14 million neem trees growing in India. The country has the potential to produce 3.5 million tonnes of seed/year, corresponding to a production of 0.7 million tonnes of oil per year (Nicoletti et al., 2012).

Neem seeds contain about 45% brownish-yellow coloured oil, mainly constituted of oleic acid (50-60%), palmitic acid (15-19%), stearic acid (14-19%), linoleic acid (8-16%) and characterized by an acrid taste and a persistent unpleasant odour (Mongkholkhajornsilp et al., 2004). The essential oils reported are hexadecanoic acid (34.0%), oleic acid (15.7), 5, 6-dihydro-2, 4, 6-triethyl-(4H)-1, 3,
5-dithiazine (11.7), methyl oleate (3.8), and eudesm-7 (11)-enol, (Kurose and Yatagai, 2005). Many other constituents reported, include pigments, polysaccharides, salts and the proteinaceous material that makes up the cellular matrix of the seeds (Johnson and Morgan, 1997). More than 300 compounds have been characterized from neem seeds, with over 50 different bioactive constituents from various parts of neem tree. One-third of reported constituents belong to the class of nortriterpenes, and more precisely to the steroid like tetranortriterpenoids, named limonoids. Neem limonoids belong to nine basic structures: azadir (from seed oil), gedunins (from kernels), salannin (from fresh leaves and seeds), and azadirachtin (from seed oil).

Limonoids are exceedingly bitter and have attracted global attention for their insecticidal, fungicidal and nemicidal properties (Gajalakshmi and Abbasi, 2004). Multiactions against insects include toxicity, antmitotic effects, antifeedant activity, growth regulation, fecundity suppression, sterilization, oviosition repellence, including harmful effects on endocrine system and damages to the cuticle of larvae preventing them from moulting (Mulla and Su, 1999). Neem extracts and oil have been tested for wood protection by Dhyani, (2008). Fumigants of Neem oil have also been tested successfully by Pant (2010) for short term protection of wood. Marked anti-fungal activity of neem seed oil against white *(Trametes versicolor* L. ex Fries) and brown rot *(Oligoporus placentus* Murr.) fungi has been reported by Dhyani and Tripathi (2004). Neem seed oil has also been found very effective in controlling termite attack by Akpan, 2001; Venmalar and Nagaveni, 2005; Dhyani and Tripathi, 2009; Olufemi et al., 2011; Sharma et al., 2011; Thlama, et al., 2012; Djenontin et al., 2012.

1.7 Thermal wood modification

Wood modification/heat treatment represents a process that is used to improve the properties of wood and this modified material can be disposed off at the end of a product’s life without presenting any environmental hazard. Modification of wood can involve active modifications, which result in change of the chemical nature of the wood substrate or passive modifications, where change in properties is affected without any alteration in the chemistry of material (Hill, 2006). Thermal wood modification though mainly used for dimensional stability had shown good results in wood protection. Thermal wood modification is not all together new technology;
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Tiemann (1920) used higher temperatures to decrease wood EMC. Thermal wood modification was not considered important because plenty of high quality durable wood species were available and research remained in passive state for nearly half a century. With the decrease in durable wood species and environmental pressure, it is being explored extensively for nearly last twenty years. Many attempts were made in this direction and mainly five methods of thermal wood modification got recognition. These methods differ in heat transfer medium, temperature and time of treatment. Finnish ThermoWood® uses water vapour to create protective atmosphere for prevention of wood from burning and cracking (Jamsa and Viitaniemi, 2001). Plato process (developed in Netherland) consists of two stage Hydro-thermolysis and dry curing, with an intermediate drying operation (Militz and Tjeerdsma, 2001). German Menz Holz process uses hot vegetable oil bath for heating (Rapp and Sailer, 2001). WTT Thermo treatment process (developed in Denmark) treat wood in a pressurized atmosphere at 3-19 bars and uses pre-dried wood (WTT, 2011). In France, two modification processes are in use. In Le Bois Perdure, fresh wood is dried and further treated in a heated steam which is generated during drying, while in retification process seasoned wood is heated under nitrogenous atmosphere (Verinois, 2001). The success of treatment depends upon the treatment time, temperature and wood species. The average range of temperature is 150°C to 260°C, below 150°C there is only drying and slight changes and above 260°C pyrolysis of wood takes place.

1.7.1 Changes due to thermal treatment

Several reports dealing with the properties of heat-treated wood have been published (Stamm et al., 1946; Tjeerdsma et al., 1998; Militz, 2002; Bekhta and Niemz, 2003, Esteves and Pereira, 2009). The main advantage of heat-treated wood is reduction in hygroscopicity and improved dimensional stability. Additionally, the resistance of wood to biological attack appears to be improved after heat treatment (Kamdem et al. 2002; Boonstra et al., 2007; Borrega et al., 2009). Decrease in mechanical properties, together with an increased brittleness, are the main drawbacks of heat-treated wood (Esteves et al., 2007; Kocaefe et al., 2007; Korkut et al., 2008), limiting its use to applications, where good mechanical properties are not required. The poor mechanical performance is largely caused by degradation of chemical constituents like hemicellulose, cellulose and lignin (Esteves et al., 2007).
The exposure of wood to elevated temperatures during heat treatment induces thermal degradation of the wood. At temperatures above 100°C, chemical bonds in wood begin to cleave. Hemicelluloses are the least thermally stable polymers of the wood structural components (Bourgois and Guyonnet, 1988, Alén et al., 2002). Thermal stability of hemicelluloses is lower than cellulose, possibly due to their lack of crystallinity, branched structure, and lower degree of polymerization (Alén et al., 1996, Garrote et al., 1999). Lignin, owing to its structural diversity, degrades gradually over a wider range of temperatures than carbohydrates (Stamm, 1956). The extent of thermal degradation is much dependent on the wood species and on the heat treatment conditions. Since hardwoods contain a higher proportion of hemicelluloses than softwoods, they are degraded more extensively when subjected to elevated temperatures (Zaman et al., 2000, Kamdem et al., 2002). The presence of air (oxygen), acids, and water in the heating atmosphere also affect the thermal degradation of wood. In the presence of air, degradation of wood components is greater than in inert atmosphere because of oxidation reactions (Stamm, 1956; Mitchell, 1988; Hill, 2006a). Organic acids, mainly acetic acid, released during the heating of wood catalyze the hydrolysis of wood components, in particular carbohydrates (Garrote et al., 1999; Sundqvist, 2004; Tjeerdsma and Militz, 2005). The degradation of wood is much faster in the presence of moisture (steam or liquid water) than in a dry condition (Stamm 1956; Mitchell, 1988), because in hydrothermal processes, hydronium ions generated (through water auto-ionization) accelerate the cleavage of acetyl groups linked to the hemicelluloses, with the consequent formation of acetic acid (Garrote et al., 1999; Garrote et al., 2001; Sundqvist, 2004; Tjeerdsma and Militz, 2005).

The degradation of hemicelluloses comprises deacetylation and depolymerization reactions to form oligo- and monosaccharides (Sundqvist, 2004; Tjeerdsma and Militz, 2005). The monosaccharides may then be dehydrated into degradation products such as furfural or 5 hydroxymethylfurfural, depending on whether the sugar unit is pentose or hexose, respectively (Tjeerdsma et al., 1998; Weiland and Guyonnet, 2003). Cellulose crystals are hardly degraded by thermal treatments at temperatures below 300°C (Kim et al., 2001). However, degradation of amorphous cellulose, resulting in an increase in observed cellulose crystallinity, has been reported to occur during heat treatment of wood (Sivonen et al., 2002; Wikberg...
Thermal treatments also induce cross-linking reactions within the lignin complex (Tjeerdsma et al., 1998; Nuopponen et al., 2004; Wikberg and Liisa Maunu, 2004). On a microstructural level, the removal of wood components due to thermal degradation is assumed to create cavities within the wood cell wall, as demonstrated by an increase in pore size (Hietala et al., 2002).

Thermally modified wood is reported to be vulnerable to different biodegrading agents, like marine borers (Westin et al., 2006), termites (Doi et al., 1999). Termite susceptibility is a major problem with heat treated wood, which renders it usage in areas where termites are one of the main wood destroying agencies (tropics and subtropics mainly). As termites are main problem in most parts of India, heat-treated timber may not be suitable unless some termite protection measures are taken. Further use of thermally modified wood in ground contact is not recommended (Kamdem et al., 2002). Therefore, there is need to develop an eco-friendly method which can provide protection to thermally modified wood in tropical conditions without affecting ecosystem.

OBJECTIVES OF THE STUDY

1. Improvement in durability of non-durable wood by heat and neem seed oil treatments.
2. Improvement in dimensional stability of wood.