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REVIEW ON THERMAL TREATMENTS OF WOOD

Jieying Wang
Post-doc research fellow

Paul Cooper
Professor
Faculty of Forestry, University of Toronto
Toronto, Canada M5S 3B3

Abstract

Thermal modification of wood mainly aims to improve the dimensional stability and the biological resistance of wood, without serious reduction of the mechanical properties. Compared with the wood treatments with preservatives or other chemicals, heat treatments of wood have the environmental advantage of being pesticide-free. In recent years, several wood thermal treatment processes have been commercialized in Europe. This paper reviews the main processes of wood thermal treatments in the industry, and the corresponding wood property changes. It also discusses the chemical changes of the three main components of wood cell walls during heat treatments and the various influences caused by oxygen, moisture and inorganic chemicals. In addition, the paper tries to put forward some ideas for further research on improving heat treatment processes and on clarifying the chemical changes of wood during heat treatments.

Keywords: Wood, thermal treatments, dimensional stability, biological resistance, mechanical properties, chemical changes.

Introduction

Heat treatments (or thermal treatments) of wood are very traditional in the wood industry. They are used to dry wood, decrease growth stresses, fix wood set (wood deformation caused by certain stress then temporarily fixed by low moisture content (MC) and low temperature, such as wood compression set), accelerate some reactions in wood and sterilize wood. (Norimoto 1994). As a modification method to improve wood properties, wood thermal treatments mainly aim to reduce the hygroscopicity, improve the dimensional stability, and enhance the resistance against biological attack. As early as in the 1920's, reports have shown that wood exposed to high temperature for some time will have lower hygroscopicity and lower shrinkage (Tiemann 1920, 1951; Stamm and Hansen 1937; Seborg et al. 1953; Stamm and Harris 1953; Stamm 1964; Burmester 1973; Giebeler 1983; Feist and Sell 1987; Wang et al. 2000a). Wood heat treated beneath the surface of molten metals, oils or fused salts was called Staybwood by the U.S. Forest Products Laboratory (Tiemann 1951, p.192; Stamm and Harris 1953; Stamm 1964). In addition, research confirmed that heat treatments also improve the biological durability of wood (Stamm and Harris 1953; Stamm 1964). Since chemical preservatives of wood, such as creosote and CCA, are pesticides and raise some concerns about their environmental and health safety, their uses as wood preservation are restricted in more and more countries. It is necessary to explore approaches to wood modification without toxic chemicals to evaluate its potential to partially take the place of wood preservation. In recent years, thermal modification of wood has been carried out successfully on an industrial scale in Europe. This review summarizes the main processes of wood thermal modification in industry and the corresponding wood property changes, it also emphasizes the chemical changes of the main components of wood cell walls and the various influences of oxygen, moisture and inorganic chemicals during heat treatments.

Main processes of wood heat treatments in the industry

Process comparisons

Up to now, there are five typical processes of wood heat treatments on an industrial scale (Kamdem 2002a). They are the oil-heat treatment in Germany (OHT-Process) (Sailor et al. 2000a, 2000b; Rapp and Sailer 2001; Militz 2002a, 2002b; Welzbacher and Rapp 2002), Thermo Wood (or Premium wood) in Finland (Syrjänen and Kangas 2000; Syrjänen 2001; Jämsä 2001; Militz 2002a, 2002b; Welzbacher and Rapp 2002), Retification process (New Option Wood) and Bois Pserdure in France (Dirol and Guyonnet 1993;Vernois 2001; Militz 2002a, 2002b; Welzbacher and Rapp 2002; Jermannaud et al. 2002), and Plato process in Netherlands (Tjeerdsma et al. 1998a, 1998b, 2000; Militz and Tjeerdsma 2001; Boonstra et al. 1998; Militz 2002a, 2002b; Welzbacher and Rapp 2002). The total production capacity of heat-treated wood in 2001 was estimated as about 165,000 m^3 (Militz 2002a, 2002b). These processes are summarized in Table 1. The OHT-Process is carried out in a closed vessel, with hot crude vegetable oil circulating around the wood during the treatment. In the process of Thermo Wood, fresh wood is first dried to the MC of nearly zero by elevating the temperature to 100C quickly, then to 130 C steadily. Then the heat treatment of wood in steam evaporated from wood, the subsequent cooling, and the conditioning steps are carried out, respectively. The Retification process treats air-dry wood in a specific vessel at high temperatures and in a nitrogen atmosphere with less than 2% of oxygen, while the Bois Perdure process starts with fresh wood, which is subjected to fast drying and high-temperature treatment under a steam atmosphere. The Plato process combines a hydrothermolysis step with a curing step, with an intermediate drying operation. During its hydrothermolysis step, green or air-dry wood is treated at temperatures ranging from 160C to 190C under increased pressure, then the wood is dried to a low MC, followed by the dry curing step at temperatures ranging from 170C to 190C (reviewed in Militz 2002a, 2002b). In common, all these processes require accurate control of high temperatures for a given length of time to improve some of the wood properties. The duration for the heat treatment step may last a few hours or longer, depending on the processes, the species and the purposes of the treated wood. The main differences among the five processes are their heating media (Table 1). The OHT-Process cooks wood in crude vegetable oil, Thermo Wood treats wood in steam, while the Retification process uses nitrogen as the shielding gas. Concerning the processing steps, the Plato process has a characteristic step of “hydrothermolysis” before the dry curing step.

Table 1. *Comparison among the five wood heat treatment processes*

	Media	MC of wood	Treatment temperature (C)	Steps	Approximate cost (Euro/m^3)
Oil-heat treatment (OHT)	Hot oil	Air-dry, e.g., 6%	180-220	One step	65-95
Thermo Wood	Steam	Fresh wood	150-240	Three steps (Temperature rising and drying, heat treatment, then cooling)	
Retification process	N_2	Air-dry, e.g., 12%	200-240	One step	150-160
Bois Pserdure	Steam	Fresh wood	200-240	One step	100
Plato process	Steam or air	Green or air-dry wood	170-190	Hydrothermolysis, drying, then curing	100

Properties of heat-treated wood

Dimensional stability and hygroscopicity.—Most impressively, reports show that all the heat-treated wood has lower hygroscopicity and higher dimensional stability. For Staybwood, antishrink efficiencies (ASE) of 40% to 50% can be obtained by either heating at 320ºC for 1 min or at 150ºC for 1 week, and the required temperature decreases linearly with the increase of the logarithm of the time for a given degree of dimensional stabilization (Stamm and Harris 1953; Stamm 1964). In Europe, wood heat-treated in oil at 220C for 4 hrs had a fibre saturation point of 14%, compared with 29% for the untreated samples (Rapp and Sailer 2001). For the Thermo Wood process, the wood has reduced swelling by about 80% to 90%, while its equilibrium moisture content (EMC) is reduced by 40% to 60% (Syrjänen and Kangas 2000). Slight pyrolysis of wood in nitrogen at the temperatures of 180 C to 220 C imparted an EMC of 4-5% to wood, compared to 10-12% before the treatment (Vernois 2001), and the corresponding dimensional stability of wood was improved by about 50% (Jermannaud et al. 2002). Wood treated by the Plato process, obtained swelling (or shrinking) reduction ranging to about 50%, generally with the higher reduction in the tangential direction than in the radial direction, which makes wood less anisotropic in swelling or in shrinking (Tjeerdsma et al. 1998b; Militz 2002a, 2002b). On the other hand, unlike for the adsorption properties, the treated wood may have higher water absorption (Vernois 2001), larger pore sizes and broadened pore size distribution, and higher diffusion coefficient of water along the tracheid axis (Hietala et al. 2002).

Actually, the hygroscopicity of wood may decrease even in low-temperature drying. There is the physical phenomenon of “sorption hysteresis” of wood. Generally it is explained to be caused by the formation of hydrogen bonds among the hydroxyls of components in wood cell walls during desorption, so these water sorption sites are not able to adsorb the same amount of moisture during the subsequent sorption (Siau 1971). However, the reduction of EMC during the sorption hysteresis is very low, compared with that resulting from high temperature treatment, and the sorption hysteresis disappears at certain higher temperatures (Skaar 1988). Meanwhile, some Japanese researchers (Obataya et al. 2000) found that the reduced EMC of wood treated at high temperatures recovers, i.e., the EMC increases to a certain degree when exposed to high humidity atmosphere or to water. They attributed this recoverable hygroscopicity to the formation of some physical structures during heating and explained the irrecoverable part of the reduced hygroscopicity with chemical changes in the matrix (In Japanese literature, "matrix" is usually composed of lignin and most of hemicellulose in wood cell walls, contrary to "microfibrils" of cellulose with high crystallinity (Norimoto 1993)). Moreover, Higashihara et al. (2001) tried to explain that the heat fixation of compressed wood is mainly caused by the formation of some "cohesive" structure (i.e., some kind of physical structure in polymers, but it is not clearly clarified in the paper) in wood cell walls, while considering the heat decomposition of the main components in wood cell walls only as the minor reason for the fixation. However, most of the related references indicate that the dimensional stabilization of high temperature should be explained with some chemical changes of the main components in wood cell walls. This will be discussed below.

Resistance against biological attack.—Of great significance, it was reported early that Staybwood had considerable decay resistance compared with the untreated wood (Stamm and Harris 1953; Stamm 1964), and the heat-treated wood by the above industrial processes also has improved resistance against fungi (Militz 2002a, 2002b; Welzbacher and Rapp 2002). For the oil-heat treatment, at the highest temperature of 220 C, with the minimum consumption of oil, the wood gains the highest resistance against fungi, especially to brown rot fungi. It was also presented that the wood treated in hot oil is more resistant to *Coniophora puteana* (a species of brown rot fungus) than the wood treated in hot air, suggesting that the different media, the oil or the air (in the presence of oxygen), have different influence on physical or chemical changes of wood during heat treatments. But neither of the two treatments achieves improved durability against marine borers (Rapp and Sailer 2001; Sailer et al. 2000a, 2000b). The Thermo Wood process improves the biological resistance of wood at the temperatures higher than 220 C and longer than 3 hrs. But it does not increase the durability of wood in ground contact (Jämsä and Viitaniemi 2001). In the Retification process, the higher the temperature of the treatments, the better the durability of the treated wood. Thus, temperatures of 230~240 C are ideal for the durability, but such high temperatures significantly reduce mechanical properties of wood (Vernois 2001). Kamdem et al. (2000) detected some polyaromatic compounds in the organic extractives from thermal modified wood using GC-Mass and ^{13}C NMR, and suggested that the improved biological resistance was likely partially due to the formation of some toxic byproducts from heat treatments. They (Kamdem et al. 1999, 2002b) also reported that the heat treatment of the French process could improve the durability of wood from non-resistant to moderate or resistant species depending on the fungi (ASTM 2017), but pointed out that the treated wood was not sufficiently improved in the decay resistance to be used in ground contact without further protection. The Plato process also imparts improved durability against decay fungi and soft rot fungi, especially against brown rot fungi. Its process with hydrothermal treatment gives wood more improved resistance against fungal deterioration, and the condition of the hydrothermolysis has more effects on soft rot and brown rot decay, while the condition of the curing step has more effects on white rot decay (Tjeerdsma et al. 2000, 1998b; Militz and Tjeerdsma 2001). According to the investigations from Welzbacher et al. (2002), the Plato wood and the oil-heat treated wood can be classified as "durable", the Premium wood and the Retified wood can be classified as "moderately durable" (according to EN 350-1), but there are only slight differences in the mass loss during decay tests among the four processes. By comparison, Viitanen et al. (1994) achieved better results of decay resistance of wood from heat treatments in a lab oven, with the best results comparable to those from CCA-impregnated wood.

And the Retified poplar can even become highly resistant so that the soft rot fungi are not able to decay the wood (Dirol and Guyonnet 1993).

In general, the durability of heat-treated wood depends on wood species and heat treatment conditions. It is believed to be closely associated with the EMC reduction since certain MC of wood is necessary for the growth of fungi (Stamm and Harris 1953; Stamm 1964). Although it was reported that the improvement of durability of sugi wood [*Cryptomeria japonica* D. Don] treated in liquid paraffin at 90 C to 150 C was attributed to the coating of paraffin on the wood surfaces, not due to the heat treatment (Matsuoka et al. 2002), the chemical changes of the wood components during treatments at higher temperatures or for longer time could still be the main reason for the durability changes. And for the oil-heat treated wood, the oil absorbed by wood during treatment may have some effects on the biological resistance of wood.

Mechanical properties.—Thermal degradation of wood can start at temperatures below 100 C if wood is heated for enough time. Youngs (1957) found most of the mechanical properties or rheological properties of wood in the transverse direction were significantly affected by the heat treatment at 82 C for 30 days, and wood may lose 10% of its original MOE heated at 120 C for about one month (Shafizadeh and Chin 1977), and solid–sawn and composite lumbers can lose more than half of their MOR after exposure to temperature of 66 C or 82 C with different relative humidities for several years (Green et al. 2003). On the other hand, it was reported that mild heat treatments at temperatures ranging from 140 C to 200 C, within certain time limit increase the MOR and MOE of wood (Dwianto 1999a; Santos 2000), which could be attributed to the slight increase of crystallinity in wood cell walls (Dwianto 1999a). However, for improving dimensional stability or biological resistance of wood, or for fixing compressed wood or bent wood, much more severe heat treatments with higher temperatures and longer durations are required (Dwianto et al. 1997), which may cause serious chemical degradation of the components in wood cell walls, leading to the drastic reduction of the mechanical properties of wood, especially the toughness, abrasion resistance and MOR (Stamm and Harris 1953; Mitchell 1988). The reduction of the mechanical properties depends on the temperature, time, heating media of the heat treatments, the species and so on. For the Retification process, heat treatments may decrease the MOR of wood by 30% to 40% at 230 C (Vernois 2001), or by 10 to 50% at 220 C (Kamdem et al. 1999, 2002). But of great interest, the mechanical properties of the heat-treated poplar are not greatly affected (Vernois 2001). For wood treated in oil at 220 C, the MOR is about 70% of that of the untreated samples, while the MOE does not drop greatly. The impact bending strength is only about 50% of the value of the controls. By comparison, after the heat treatment in air at similar conditions, the wood samples only retain 37% of the original strength (Rapp and Sailer 2001; Sailer et al. 2000b). For the hardness of wood, a reduction of 21% at ASE of 40% and a reduction of 33% at ASE of 60% for wood heat-treated in the absence of air were reported (Stamm and Harris 1953). Obviously, the greatest disadvantage of heat treatments is the reduction of the mechanical properties of wood. It limits the application of heat-treated wood for many structural purposes.

In order to predict the property changes of wood during heat treatments, some isolines have been developed. Stamm et al. found the linear isolines of ASE for Staybwood with logarithm of time as the Y-axis and temperature as the X-axis (Stamm and Harris 1953; Stamm 1964). Shafizadeh and Chin (1977) presented the isolines of MOE loss in the same plane of coordinates for heat treatment of wood. Millett and Gerhards (1972) achieved the relationship between time and reciprocal of absolute temperature during heat treatments for wood specimens to attain various residual MOR, MOE or residual weight. The authors (Wang et al. 2000a) put forward the isolines of weight loss and dimensional stability for uncompressed wood, and the isolines of recovery of compression set for compressed wood during heat treatments. It will be of great significance if the isolines of mechanical properties of wood during heat treatments under different conditions, especially under different media of heating, can be established.

Other properties.—After heat treatments, wood with light colour will have typical colour changes to light brown, even to dark brown, depending on the treatment conditions and its original colour (Bekhta and Niemz 2003). But such colour can still be acceptable, even could be considered better than the original colour for some species and for some purposes. Some spotted discolorations due to exudation of rosins will often appear on the surfaces of wood after heat treatments in steam or in nitrogen, but it is reported that there are no such spots on the oil-heat treated wood (Rapp and Sailer 2001). For some species susceptible to sap stain, the discolorations will disappear after the Retification process (Jermannaud et al. 2002). The heat treated wood also gives off a characteristic smell, which will last for some time and could be attributable to the release of furfural during heating (Militz 2002a, 2002b). In addition, the UV-resistance, wettability (Petrissans et al. 2003), paintability and gluability of heat-treated wood may change in a certain degree. Jämsä et al. (2000) studied the performance of the coated heat-treated and untreated panels during exterior exposure for five years, and the main results are: Without coating the heat-treated wood is not weather resistant, but such weather resistance can be improved by the water- or solvent-borne paints, and the heat-treated wood almost retains the same paintability as the untreated wood.

Chemical changes of wood during heat treatments

Generally speaking, wood begins to degrade obviously at the temperature of about 165 C (Stamm and Hansen 1937). Among the three main components of wood cell walls, hemicellulose decomposes much faster than cellulose, and cellulose decomposes faster than lignin (Stamm 1964). Hemicellulose decomposes drastically at temperatures ranging from 225 C to 325 C, while cellulose has the most severe decomposition reactions at 325-375 C, and lignin decomposes gradually at the temperatures ranging from 250 C to 500 C, and most drastically at 310-420 C (Shafizadeh and Chin 1977). Due to the variety of wood species and the great variation of their properties, and the different conditions of heating and testing, the data from literature are not in good agreement. For example, it was also reported that the most drastic decomposition of hemicellulose, cellulose and lignin takes place at the temperature ranges of 180-300 C, 240-400 C and 280-550 C, respectively (Kuriyama 1967). The three components behave differently during heat treatments since they have different structures and different distributions in wood cell walls, which also decide their functions in wood properties. For example, they affect the biological resistance against various fungi. As for the hygroscopicity and the dimensional instability of wood, hemicellulose should have the most important contribution due to its highest hydrophilicity among the three components (Rowell 1984, p. 139).

Some scientists had suggested that the reduced hygroscopicity of wood during heating is due to the formation of some ether linkages between adjacent cellulose chains. But later studies showed this did not occur as ether linkages should be resistant to sodium hydroxide (NaOH), pyridine, or morpholine but heat treated wood swelled as much as untreated wood in these solvents while by comparison, formaldehyde cross linked wood had reduced swelling. Another common assumption was that thermal decompositions or transformations of wood, caused the formation of furfural, a less hygroscopic substance from hemicellulose (Stamm and Hansen 1937; Seborg et al. 1953; Stamm and Harris 1953; Stamm 1964). Furfural does arise from the pyrolysis of cellulose or hemicellulose (Bourgois et al. 1988; Dirol and Guyonnet 1993). However, it is argued that furfural is unstable in the reaction mixtures and its amount is not high enough to be so critical for the wood properties (Bourgois et al. 1988).

Another hypothesis is that there is auto-cross linking of wood fibres during heat treatments (Back 1967; Back 1987). It is proposed that auto-cross linking reactions occur primarily in lignin, mainly resulting in hemi-acetal bridges. The proposed time needed for the auto-cross linking reactions is: about two weeks at 70ºC, about two minutes at 200ºC and a few seconds at 350ºC, and the most suitable condition is at 320ºC for 10 to 15 s. It can be inferred that such reactions of wood components occur faster than the decomposition reactions during heat treatments. It is also reported that auto-cross linking reactions can be catalyzed at a low PH and in the presence of metal ions with high redox potentials such as $FeSO_4$ or $Al_2(SO4)_3$ (Back 1987). Such cross linking is a kind of non-conventional bonding of wood and can be realized between activated wood surfaces under certain conditions, including higher temperature (Rowell 1984, p. 349-361).

For the above thermal modification processes in industry, the chemical changes of wood cell walls during different processes may vary, depending on the species, heating media, temperature, time and MC of wood. It is considered that during the Retification process, heat modifies the physico-chemical structure of wood, hemicellulose decomposes, and its byproducts condense and polymerize on the lignin chains (Jermannaud et al. 2002). A relatively complete theory of the chemical changes during heat treatments of wood is presented for the Plato process (Tjeerdsma et al. 1998a; Militz and Tjeerdsma 2001): During the step of the hydrothermolysis, some carboxylic acids, mainly acetic acid, are liberated from hemicellulose. They further catalyse the cleavage of other carbohydrates, producing formaldehyde, furfural and so on. Lignin also degrades and simultaneously begins to auto-condense to form some methylene bridges. In the subsequent dry curing step of the process, mainly cross-linking of methylene bridges connecting aromatic rings could take place. These chemical reactions can explain the improved dimensional stability and biological resistance of the treated wood.

Changes of hemicellulose

Undoubtedly, hemicellulose undergoes chemical changes easily and quickly during heat treatments of wood, which is most important for the results of treatments. Hemicellulose (especially its arabinose) even degrades severely during long-term exposure to temperatures lower than 100 C, which greatly reduces the flexural properties of lumber (Green et al. 2003). It was found that water and acetic acid are the predominant products from slight pyrolysis of wood, plus some methanol, formic acid and furfural (Bourgois et al. 1988; Dirol and Guyonnet 1993; Militz and Tjeerdsma 2001). Much of the acetic acid should be attributed to the decomposition of hemicellulose, especially to hemicellulose with acetyl groups (Browne 1958; Bourgois et al. 1988; Sivonen et al. 2002). During heat decomposition of beech with restricted air supply, it is analysed that the pentosan content decreases by 8% at 171 C and decreases by up to 20% at the elevated temperature of 206 C. At temperatures ranging from 245 C to 275 C, 45% of the pentosan and 40% of the acetyl groups were decomposed or separated (Sandermann and Augustin 1964). The existence of acid and water in wood may further accelerate the hydrolysis of the wood cell wall components, especially hemicellulose. It is known that hemicellulose has various structures with pentoses, hexoses and other groups, the behaviours of these groups vary to a certain extent during heat decomposition. Generally, hemicellulose of hardwoods is more unstable than that of softwoods (Kamdem et al. 1999, 2002; Bourgois et al. 1988), which could be attributed to the higher acetyl groups in hardwoods, instead of the higher content of pentoses (Green et al. 2003), which should also be the reason why softwoods are usually heat treated more strongly than hardwoods in the industry (Syrjänen and Kangas 2000; Syrjänen 2001). For the heat decomposition, investigations show that after slight pyrolysis, the element proportions in wood cell walls change a lot: the hydrogen and oxygen decrease, while the carbon ratio increases greatly (Bourgois et al. 1988; Dirol and Guyonnet 1993), and it is clear that hemicellulose is most rich of hydrogen or oxygen in wood cell walls. In addition, it should be noted that the treated wood shows a rapid drop in hydrophilicity from the beginning during heat treatment (Bourgois et al. 1988). Compared with heat stabilization of wood, heat treatments of paper cause less strength loss due to less hemicellulose present in paper (Stamm 1964). On the other hand, concerning the mechanical properties of wood, Curling (2001) proved that the loss of hemicellulose during incipient brown rot decay of southern pine led to high levels of strength loss, and the significant loss of glucan (representing cellulose) was barely detected until more than 75% of the original MOR was lost, and the MOR loss appeared to occur at a greater rate than the MOE loss, which is in good agreement with the phenomena found in wood heat treatments at lower temperatures (Green et al. 2003).

Hence, it seems reasonable that the increase of dimensional stability and biological resistance, and the reduction of mechanical properties during heat treatments are mainly attributed to the breakdown of hemicellulose, the most hydrophilic and the most unstable polymer in wood cell walls. It should not be the simple cleavage reactions that take place in hemicellulose, and the degradation products from hemicellulose are not confined to furfural only, there could be some cross-linking and polymerization reactions associated with hemicellulose taking place during heat treatments of wood.

Changes of lignin

In general, lignin is considered resistant to high temperature. During heat treatments, the lignin content and the carbon content in wood increase (Bourgois et al. 1988; Dirol and Guyonnet 1993), especially for hardwoods with higher contents of hemicellulose (Kamdem et al. 1999, 2002). During pyrolysis, lignin produces more charcoal than cellulose and hemicellulose (Browne 1958), and it was reported that after “torrefication” of sawdust at 260 C for 4 hrs, lignin increases from 28% to 84%, analysed by sulphuric acid method (Bourgois et al. 1988). Although lignin is relatively hydrophobic and inactive in chemical reactions due to less hydroxyl groups, it has methoxyl groups, and it was also reported that the ether linkages in lignin are easier to cleave during pyrolysis (Browne 1958). From 200ºC to 250ºC, carbon dioxide and other compounds are liberated from lignin, from 250ºC to 400ºC, phenolic and neutral oils etc. are produced, some of which tend to polymerize, and the thermal decomposition of lignin becomes exothermic at about 270ºC (Stamm and Harris 1953, p. 66). Tanahashi et al. (1982, 1989) found some brown oily materials and also fibrillar cellulose in wood after explosion with high-pressure steam at 230 C, in which the degradation of lignin was believed to play an important role. In the research for mechanisms of permanent fixation of wood compression set with high-temperature steam treatments or heat treatments, it is considered that the cleavage of hemicellulose, lignin and even some microfibrils lead to stress relaxation and increased hydrophobicity (Norimoto 1993, 1994; Dwianto 1998, 1999a, 1999b; Wang 2000b). Kamdem et al. (1999, 2002) found the by-products of lignin from Retified wood and suggested that it was the degradation of lignin rather than the cross-linking reactions that takes place in lignin during heat treatments. Analogous to this, during weathering, it is mainly the lignin in wood cell walls that absorbs the energy from ultra violet light then degrades, which indicates that lignin is not highly resistant to degradation. In addition, it is possible that the serious decomposition of hemicellulose and the somewhat acidic environment in wood cell walls during heating make lignin, which is believed to be closely associated with hemicellulose, degrade to a certain extent during heat treatments.

There is also some evidence of condensation reactions taking place in lignin during heating. During the thermal decomposition of beech with restricted air supply, at the temperatures ranging from 245 C to 275 C, a transformation of lignin, which was considered as a condensation rather than a thermal decomposition occurred, and in its extract, only traces of phenolic substance could be tested (Sandermann and Augustin 1964). Funaoka et al. (1990) found that during heat treatments of wood at the temperatures from 120 C to 220 C, lignin mainly undergoes the diphenylmethane type of condensation, especially in the presence of moisture in wood. It was also suggested that after the first degradation reaction, a resinification takes place and the lignin is greatly modified during the torrefication of sawdust at 260 C (Bourgois et al. 1988). During chemical modification of wood, lignin is always substituted more easily than holocellulose and it is more reactive than cellulose toward acetylation (Rowell 1984, p. 205), and lignin seems to be the most reactive among wood components in auto-crosslinking reactions (Back 1967; Back 1987). For the thermally modified wood in Finland, demethoxylation of lignin and stable free radicals are observed and it is believed that the radicals take part in condensation reactions leading to cross links within lignin and possibly with other components present (Sivonen et al. 2002). In conclusion, during heat treatments, there are some cleavage reactions in the weak points of lignin, and there are also some condensation reactions associated with lignin and also with some breakdown products from the main components of wood cell walls.

Changes of cellulose

It is well known that cellulose in wood cell walls is relatively stable owing to its high polymerization degrees and high levels of crystallinity. During pyrolysis of cellulose, only insignificant decomposition takes place before 257 C and its IR and X-ray spectra remain unchanged, although the numbers of carboxyl and carbonyl groups increase a little (Sandermann and Augustin 1964). Bourgois et al. (1988) also proved that cellulose did not undergo noticeable modifications in its crystallinity during torrefication of wood sawdust at 260 C by studying its X-ray spectra. Beall (1969) indicated that cellulose did not degrade obviously until the decomposition of hemicellulose was nearly over. However, Browne implied (1958) that some of the carbon-to-oxygen bonds in the links between glucosan units of cellulose might cleave along the chains early in the pyrolysis, especially in the presence of water and some acids, and levoglucosan was the characteristic product of the primary pyrolysis of cellulose. Tanahashi et al. (1982, 1989) suggested that during wood explosion with high-pressure steam at 230 C, the length of microfibrils decreased as the result of scission of cellulose chains in some amorphous regions. In addition, the stability of cellulose may be reduced somewhat because of its proximity to hemicellulose (Beall 1969) and in the presence of some acids. Moreover, it was reported that during heating of wood at 180 C, some â-cellulose in cell walls condensed into á-cellulose, or fragmentized into ã-cellulose, resulting in the redistribution of the polymerization degrees of cellulose in wood cell walls (Kuriyama 1967).

Cellulose and lignin in wood cell walls have much lower hygroscopicity than hemicellulose (Rowell 1984, p. 139). It must be infeasible for cellulose or lignin to be degraded greatly during any type of wood treatment, due to their great contribution to the physical and mechanical properties of wood. If some local cross-linking reactions occur in lignin or in the amorphous regions of cellulose, with very limited degradation, the biological durability and the dimensional stability of the whole wood could be improved, with less reduction of the mechanical properties. Hopefully such reactions can be realized under certain conditions of temperature and time of the heat treatments, possibly in the presence of some chemical additives.

Effects of oxygen on heat treatments of wood

Studying the effects of oxygen on wood heat treatments is of great significance, since it must be easier and cheaper to carry out the wood modification in air, in the presence of oxygen. On the other hand, if oxygen is beneficial to wood heat treatments, we can supply air even oxygen to accelerate the treatments, just like what we do to accelerate burning of wood. But actually, according to the heat processes in Europe, wood can hardly be heat treated in the presence of oxygen since the negative influence of oxygen on the biological resistance and mechanical properties of wood (Rapp and Sailer 2001; Sailer et al. 2000a, 2000b). The pioneering heat treatments of wood (Stamm and Hansen 1937; Seborg et al. 1953; Stamm and Harris 1953; Stamm 1964) show that oxidation is not essential to dimensional stabilization of wood during heat treatments since improved ASE can be obtained in hydrogen, while higher ASE is obtained in oxygen than in reduced pressure of air, and it seems that ASE is proportional to the darkness of the samples. For Staybwood, the treatment is carried out in the absence of oxygen to prevent the great loss in strength. It was also reported that the presence of air during wood heat treatments leads to higher ASE, higher weight loss for uncompressed wood, lower recovery for compressed wood, and oxygen acts like a catalyst for the changes of wood components during heating (Dwianto et al. 1997; Wang et al. 2000a). Sandermann and Augustin (1964) studied the influence of oxygen or nitrogen on pyrolysis of cellulose and found no essential difference between the two gases in the course up to the temperature of 331 C, but on the whole, lower weight loss and lower carbonyl content were obtained in nitrogen than in air, hence oxidation must take place at lower temperatures. Similarly, TGA (thermo-gravimetric analysis) also shows that the initial period of degradation is faster in air than in nitrogen during pyrolysis of cellulose, but as the temperature increases, the initiation period and the difference between in nitrogen and in air gradually diminish, and finally disappear at the temperature of about 310 C (Rowell 1984, p. 492). Beall (1969) found that the initial degradation temperatures of hemicelluloses with different sources were lower in oxygen than in nitrogen, and the maximum rates of degradation were higher in oxygen. Mitchell (1988) tried to characterize the role played by atmospheric oxygen and wood moisture in the thermal degradation of Loblolly pine at 150 C, in the duration of 1 hr to 16 hrs, and found that the effects of oxygen on thermal degradation of wood depended on the MC of wood, with greater effects on oven-dry specimens, and oxygen had more influence on MOR and MOE than on reflectivity of wood surfaces. He also pointed out that oxygen had no significant influence on the specific gravity and hygroscopicity of wood, which seems conflicting with some other results (Wang et al. 2000a).

On the other hand, isolated xylan, one of the monomers of hemicellulose, degrades differently in different media of heating. Under atmospheric pressure of inert gas, fragmentation of the xylan takes place between 225 C and 300 C, followed by dehydration and furfural production. While in vacuum, cross-linking of xylan fragments apparently prevents the formation of furfural, meanwhile some hydride compounds are formed and evaporate at the temperatures ranging from 220 C to 300 C (Beall 1969). This report suggests that the different media and pressure during heat treatments may have essential influence on the chemical changes of wood. But it is not clear how oxygen affects the reactions of degradation or cross-linking of the wood components.

The above discussions come down to some questions to be clarified in the future. Does oxygen really accelerate the chemical reactions of all the three cell wall components? Which reactions does it primarily affect? Does oxidation affect the crystallite region of cellulose greatly during such heat treatments? And the final focus is on whether oxygen has negative influence on the biological resistance and the mechanical properties of wood (Rapp and Sailer 2001; Sailer et al. 2000a, 2000b) and whether similar properties of wood, including the dimensional stability, the biological resistance and the mechanical properties can be achieved at lower temperature or for shorter time in the presence of oxygen during heat treatments of wood.

Effects of moisture on heat treatments of wood

In the processes of wood heat treatments in Europe, Thermo Wood (or Premium wood) in Finland (Syrjänen and Kangas 2000), Le Bois Perdure in France (Vernois 2001), and the Plato-Process in Netherlands (Militz and Tjeerdsma 2001) can be carried out with fresh wood, using steam as the shielding gas, and the Plato process is characteristic of the step of hydro-thermolysis before the dry curing step.

The existence of water in wood during heating must speed up the heat transfer, and accelerate the decomposition of the main components of wood cell walls, since hydrolysis is one of the easiest reactions for wood carbohydrates. During retification of wood, water and acetic acid are predominant in the liquid phase and the presence of water in wood improves the liquid emission (Dirol and Guyonnet 1993). Skaar reported that the heat degradation was 10 times faster for wet wood than for dry wood (reviewed in Yildiz 2002). Burmester (1973) found that certain moisture in wood led to higher ASE and little reduced strength of wood under certain pressure, and the optimum MC of wood for the heat treatments ranged from 20% to 30%. During kiln drying of wood, high humidity in the environment reduces the hygroscopicity of wood more than the low humidity does, while higher temperature is needed to achieve the similar reduced hygroscopicity in the case of dry wood (Hillis 1984). Mitchell (1988) compared the effects of atmospheric oxygen and wood moisture on thermal degradation of Loblolly pine at 150 C, with the time ranging from 1 hr to 16 hrs. He reported that when moist specimens were heated, hydrolysis had more influence than oxygen-dependent degradation, especially on the reflectivity of wood surfaces, MOR and MOE, possibly attributable to the more organic acids formed in the presence of water or steam. However, Mitchell also suggested that the presence of moisture in wood during heating seldom affected the residual hygroscopicity of wood, which is not consistent with the results from other researchers (Burmester 1973; Hillis 1984).

In wood cell walls, moisture does not exist in the crystallite regions, which suggests that it has less influence on the mechanical strength of wood, but it could affect the reactions of decomposition or condensation during heat treatments. Hence, the effects of moisture on wood properties, especially on the biological resistance and the mechanical properties during heat treatments should be studied more systematically in the future. In addition, it was reported that steam treatments under high pressure are much more efficient and lead to much better results than heat treatments for fixation of compressed wood (Norimoto 1994; Inoue et al. 1993; Dwianto 1999a), and steam injection is also used in wood composite pressing to improve the efficiency and product properties, hence, it is also necessary to try steam treatments of wood instead of heat treatments.

Effects of inorganic chemicals on heat treatments of wood

The effects of inorganic chemicals, especially some fire retardants on thermal pyrolysis of cellulose or wood have been studied by some researchers (Hirata and Abe 1973a, 1973b, 1973c; Hirata 1976; Hirata et al. 1978), and it is of great significance both to wood fire retardation and to heat treatments of wood. For the latter, it determines whether it is possible to catalyze the heat treatment processes with some chemicals thus to enhance the efficiency of the treatment (Stamm

1964). For cellulose, one of its main pyrolysis products is levoglucosan, which will further degrade into some flammable gases and some charcoal, but the presence of water-soluble inorganic impurities will reduce or prevent the formation of levoglucosan (Browne 1958). Shafizadeh and Chin (1977) also indicated that sme acidic additives in cellulose, hemicellulose or lignin during heating, such as phosphoric acid (H_3PO_4), diammonium phosphate ($(NH_4)_2HPO_4$), diphenyl phosphate and zinc chloride ($ZnCl_2$) significantly accelerated the production of levoglucosenone instead of levoglucosan, as a result, much more charcoal was yielded. For example, during pyrolysis of xylan of hemicellulose, the addition of $ZnCl_2$ will greatly decrease the production of tar while promoting the yield of charcoal. It is considered that a series of reactions, including dehydration, condensation and carbonization take place during the charring of cell wall polysaccharides. Hirata and Abe et al. (1973) studied the effects of some inorganic chemicals on pyrolysis of wood and ascribed the increase of the char yield of wood mostly to the cellulose, since cellulose should be the main source of tars in the absence of other chemicals. Fung (1974) found that the shrinkage in the tangential direction of wood was more affected by heat than that in the radial or in the longitudinal direction in the presence of the fire retardants of mono-ammonium phosphate ($NH_4H_2PO_4$). It also greatly accelerates the char-forming process, thus protecting the wood. Later, Fung (1976) confirmed again that levoglucosenone, instead of levoglucosan, was the major product directly from cellulose during pyrolysis of cellulose treated with H_3PO_4, at the temperatures from 350 C to 840 C, and its production decreased with increasing temperature.

It seems that the main function of the inorganic chemicals, such as $ZnCl_2$, H_3PO_4, $NH_4H_2PO_4$ and borates during wood pyrolysis, is concentrated on accelerating the formation of charcoal. Such action could be correlated to the dimensional stabilization (Stamm and Hansen 1937), also the decay resistance and the mechanical properties of the heat-treated wood.

Future research

As a modified product, heat-treated wood is at an early stage of development. Up to now its production yield in the world is still very low. Its applications are limited by the high cost, the low production scales and the reduced mechanical properties of wood. And concerning its biological resistance, generally heat-treated wood is not comparable with impregnated wood with CCA or other preservatives. However, heat-treated wood has some environmental advantages and also imparts improved dimensional stability. Hence, to determine the applications for this kind of product is very important. For example, heat-treated wood with high quality can be used for musical instruments, carving of art wares, museum decoration and so on, while treated wood with lower quality can be extended to be used for room decoration and non-structural parts of housing. If coated with some finishes with high weathering resistance, heat-treated wood should also be appropriate for doors, windows and some exterior uses. So it seems necessary to establish the quality control and product classification systems for heat-treated wood, which will accelerate the development of such a new product (Syrjänen 2001; Vernois 2001; Rapp and Sailer 2001).

For the heat treatment processes of wood, it is still worthwhile to improve the industrial processes, or to find some new processes for heat treatments, or to try some combined wood modifications, for example, the compressed wood with heat fixation, which increases the density and strength of wood, with heat stabilization as well.

Concerning the improvement of wood heat treatment processes, some basic factors affecting heat decomposition of wood, such as oxygen, moisture and some inorganic chemicals, should be further studied. They are directly associated with the processes, product properties and cost. In addition, it seems that selection of wood species may be important in thermal treatments. In the end, the physical and chemical changes of the components of wood cell walls during heat treatments, especially the chemical changes, must be studied more specifically in the future.

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