NOVEL METHOD FOR DEVELOPING HIGH TEMPERATURE WOOD HEAT TREATMENT RECIPES

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ABSTRACT

The thermal treatment of wood at high temperatures is an environment friendly and commercially viable alternative wood modification technology. In this process, wood is heated to temperatures above 200ºC. This modifies the structure of wood and improves its hardness, dimensional stability, and resistance to biological attacks compared to those of the untreated wood. Its color also becomes darker and more attractive. However, this treatment may cause a decrease in wood elasticity. Therefore, optimization of the treatment parameters is necessary for a quality product. In addition, the high temperature heat-treatment processes for wood were first developed in Europe, and the recipes used for the European species were not necessarily applicable to the North American species. Thus, adaptation of the technologies to the latter species was necessary.

The industrialists in the Saguenay-Lac-St-Jean region of Quebec brought two heat treatment technologies (Bois Perdure from France and Thermowood from Finland) to Canada. The adaptation of the technology is a very costly procedure at industrial scale. The Research Group on the Thermotransformation of Wood (GRTB – Groupe de recherche sur la thermotransformation du bois) at the University of Quebec at Chicoutimi (UQAC) which works closely with these industries developed a method for adapting the existing recipes to the North American species as well as for developing new ones for other species. UQAC is the first North American university which has such a unique research structure to carry out this type of research. The recipe development starts in a laboratory scale furnace. The high temperature heat-treatment experiments are carried out in a thermogravimetric system under different conditions until a promising set of conditions is identified for the properties sought by the industry. Consequently, the trends are identified for a given species. To determine the properties, various characterization tests (bending, dimensional stability, screw withdrawal, etc.) are done. Then, the heat treatment trials in a prototype furnace are carried out to finalize the recipe. This is followed by trials in an industrial-scale furnace for validation of the results.

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In this section, the wood thermal treatment and its impact on wood will be described. The above recipe development method will be presented in detail, and its application will be discussed.

INTRODUCTION

The most commonly used method of wood preservation is the chemical treatment, which involves the impregnation of chemical substances such as traditional oil (creosote, pentachloro-phenol) and chromated copper arsenate (CCA) into the wood [Militz et al, 1997]. Contrary to the chemical treatment, the heat treatment of the wood does not require the use of any toxic chemical agents. Therefore, this treatment has attracted a lot of attention as an alternative to chemical treatment of wood. Studies carried out with beech, pine, spruce, and poplar indicated that significant improvement in biological resistance can be achieved if the heat treated wood is not in contact with ground [Kamdem et al, 2002].

During heat treatment, wood is heated to temperatures higher than those used in the conventional drying process (above 200ºC) by contacting with a hot medium. The nature of the medium depends on the technology used. For example Perdure (France) uses hot combustion gas. Air with water vapor is used by Thermowood (Finland), and nitrogen is used for retification (France). Hot oil is the medium of choice for Menz Holz process (Germany) whereas Plato uses water vapor (Holland) [Militz, 2002; Chanrion and Schreiber, 2002].

The high temperatures result in irreversible chemical conversion (called thermotransformation) in wood contrary to the simple drying process where, upon heating wood to temperatures usually between 120-140°C, only the moisture is removed by evaporation [Amy, 1961] and the volatiles start to migrate out of the wood. The absence of moisture in wood prevents the undesirable biochemical reactions and microbiological attacks. However, the dried wood can easily reabsorb water upon exposure to humid environment. Consequently, the low temperature drying of wood does not give any protection against decay and fungi.

The thermo-transformation results in the conversion of hydrophilic OH groups to hydrophobic C-O-C ether [Tjeerdsma and Militz, 2005] and O-acetyl [Hinterstoisser et al., 2003] cross-links between wood fibers. Such cross-links reduce significantly the ability of water to penetrate into the wood [Homan et al., 2000]. Thus, heat treatment hinders decay and increases significantly the dimensional stability of wood [Seborg et al., 1953; Stamm, 1956; Hillis 1984; Dirol and Guyonet, 1993; Raimo et al., 1996; Viitaniemi, 1997; Alén et al., 2002; Pavlo and Niemz, 2003; Hakkou et al, 2006]. The decrease in the number of hydroxyl groups, accessible to water, was confirmed experimentally by Tjeerdsma and Militz [2005]. Elimination of hydroxyl groups reduces the number of potential anchor-points for fungi; but on the other hand, the wood becomes more difficult to glue [Poncsak et al., 2007]. Follrich et al. [2006] observed a significant improvement of the adhesion between the heat-treated wood surface and the non-polar polyethylene polymer. The cleavage of acetyl side groups has also been reported [Tjeerdsma and Militz, 2005; Gérardin et al., 2007; Boonstra et al., 2007].

Significant depolymerization of hemicelluloses content by hydrolysis was also reported in the literature [Fengel, 1966; Bobleter and Binder, 1980; Fengel and Wegener, 1984; Carrasco and Roy, 1992; Tjeerdsma et al., 1998; Zaman et al., 2000; Garrote et al., 2001; Pavlo and Niemz,. 2003]. The monomeric sugar units produced by the hydrolysis are dehydrated to aldehydes, namely furfural and hydroxymethylfurfural formed from pentoses and hexose sugar units, respectively [Burtscher et al., 1987; Ellis and Paszner, 1994; Kaar et al., 1991]. The decrease in pH due to the formation of formic and acetic acid promotes depolymerization [Sundqvist et al., 2004]. Hemicelluloses degrades first (between 160-260^{o}C) since its low molecular weight and branching structure facilitate a faster degradation compared to the other components present in wood [Fengel and Wegener, 1984]. Hemicelluloses are the nutrients to various kinds of fungi; therefore, they are one of the key components affecting wood decay [Fengel and Wegener, 1984].

The removal of the branched hemicelluloses increases temporarily the crystallinity index of the cellulose between 160-220°C as reported in the literature [Fengel and Wegener,1984; Dwianto et al., 1996; Bhuiyan et al., 2000; Kubojima et al., 2001; Sinoven et al., 2002].

Lignin is the least reactive of the wood components, chemical bonds within the lignin can be cleaved and phenolic groups can be formed [Runkel, 1951; Kollmann and Fengel, 1965]. Consequently, auto-condensation (ramification) of the lignin takes place in the wood [Stamm, 1956; Burtscher et al., 1987; Tjeerdsma et al., 1998; Garrote et al., 1999; Homan et al., 2000].

During the heat treatment process, many volatile organic compounds – such as alcohols, resins, terpenes, etc. – are produced and released from the wood [Manninen et al., 2002; Graf et al., 2003]. At the end of the thermal treatment, the cooling water spray can capture partially the water-soluble secondary substances with low molecular weights produced by the decomposition of various wood components.

The darker and more reddish color of the treated wood due to the formation of degradation products from hemicellulose and lignin is a visible manifestation of the thermotransformation of wood [McGinnes et al., 1984; Sehistedt-Persson, 2003; Sundqvist, 2004]. The formation of oxidation products such as quinones are also mentionned as a reason for color change [Tjeerdsma et al., 1998; Mitsui et al., 2001; Bekhta and Niemz, 2003].

As explained above, the heat treatment improves the dimensional stability and the durability of wood. However, it can cause deterioration in mechanical properties due to the degradation of wood fibers. Wood can loose part of its elasticity, consequently, it can become more rigid and fragile [Stamm 1956; Fengel, 1966; Rusche, 1973; Santos, 2000; Bengtsson et al., 2002; Chanrion and Schreiber, 2002; Yildiz et al., 2002; Poncsak et al., 2006; Kocaefe et al., 2007a; Shi et al., 2007; Kocaefe et al., 2008a, Kocaefe et al., 2008b]. The degree of deterioration of the mechanical properties is a function of the heat treatment conditions [Vernois, 2001]. Depending on process parameters, fractures can appear and cell structure [Létourneau, 2006] can be partially degraded as well. Therefore, the determination of the suitable heat treatment conditions is very important for each species and different applications. Consequently, the optimization of the heat treatment parameters is necessary for each species in order to obtain a quality product.

As mentioned previously, there are different thermotransformation technologies which are all developed in Europe. These technologies differ in furnace conception, type and condition of heating gas, and treatment schedules. Since these technologies are first developed in Europe, the recipes are also developed for European species. These have to be optimized for North American species and new recipes have to be developed. This is a very costly procedure at the industrial scale. In the experimental method developed, first small wood samples are treated in a thermogravimetric system under different conditions, and the properties of the treated samples are measured. Consequently, the trends are identified for a given species. The promising treatment procedures are then tried in the prototype furnace to narrow down the options. The last step is the testing of the most favorable ones in the industrial furnace to finalize the recipe. [Kocaefe et al., 2007b].

In parallel, numerical models for furnaces of different technologies are developed in order to facilitate the optimization [Younsi et al., 2010; Younsi et al., 2009; Younsi et al., 2008]. A validated model of a treatment furnace is a valuable tool which can be used to decrease the optimization cost as well as to improve the furnace design. In this article, the emphasis will be on the experimental method developed.

THEORY

Usually wood is already pre-dried before the high temperature heat treatment. The drying and the heat-treatment can be carried out at the same time, but this is not very economical since drying takes much longer time compared to heat treatment. The initial moisture content of pre-dried wood is usually around 8-15% at the beginning of the treatment.

During heat treatment, wood is in contact with a hot medium. Simultaneous heat and mass transfer takes place in wood which is a porous medium. The heat is transferred from bulk gas to the wood surface by convection (external heat transfer resistance). Then, it is transferred from surface to the interior of wood by conduction (internal heat transfer resistance). First, wood is heated to the evaporation temperature of water. At this temperature, water starts to evaporate. Wood contains free water, bound water, vapor, and air. The moisture content is higher in the interior part of wood than on the surface. The free water will move towards the surface by the capillary action. The bound water and the vapor are transferred by diffusion to the surface [Dietenberger 1999] (internal mass transfer resistance). Water vapor is transferred from the wood surface to bulk gas by convective mass transfer (external mass transfer resistance). When wood temperature is around 150°C (depending on the species) the thermotransformation reactions start. The reaction products are also eliminated in a similar manner.

The heat conduction is given by the Fourier equation as [Holman, 1990]:

$$q = -k \frac{dT}{dx} \tag{1}$$

where “q” is heat flux in W/m^2, “k” is the thermal conductivity in W/m K, “T” is temperature in K, and “x” is the direction of the transfer in m.

The diffusion of moisture is described Fick’s Law as [McCabe et. al., 1985]:

$$N = -D \frac{dM}{dx} \tag{2}$$

where “N” is moisture flux in kg/m^2.s , “D” is the diffusivity coefficient of water in gas in m^2/s, “M” is the moisture concentration in kg water/ m^3 wood, and “x” is the direction of the transfer in m.

Convection heat and mass transfer can be written as [Holman, 1990; McCabe et. al, 1985]:

$$q = h(T_g - T_s) \tag{3}$$

$$N = \alpha_m (M_s - M_g) \tag{4}$$

where “h” is convective heat transfer coefficient in W/m^{2}K, “α_m” is the convective mass transfer coefficient in m/s, “T_g”and “T_s” are the temperatures of bulk gas and wood surface, respectively, in K, “M”$_s$ and “M_g” are the moisture contents of wood surface and the bulk gas, respectively, in kg H_2O/ m^3 wood.

The heat and mass transfer taking place during heat treatment is more complex than given by the equations above. These equations represent the transfer in one direction. In reality, the heat and mass transfer takes place in three directions. The gas velocity is important because it affects the heat and mass transfer coefficients. Therefore, the Navier-Stokes equations have to be solved to calculate the velocity profile in the furnace. The temperature and humidity distribution in gas also have to be calculated. In addition, there are also the effects of temperature on mass transfer and moisture content on heat transfer [Luikov, 1975]. The equations describing the heat treatment are presented in another section of this book on the Modelling of Wood Heat Treatment. However, it is possible to see the principles of recipe development from the equations 1 to 4. The heat and the mass transfer depend on the temperature and the moisture gradients, respectively, existing between the wood surface and the gas.

For the heat transfer, if the temperature gradient is very small (low gas temperature, see Equation 3), it takes longer to heat the wood. The slow heating rate exposes the wood to high temperatures for a long period of time and this has a negative effect on the mechanical properties [Poncsak et al.; 2006]. If the gradient is very large (high gas temperature), the surface temperature of the wood is heated to high temperatures, but the interior of the wood is not heated at the same rate since the thermal conductivity of wood is low (see Equation 1). This can be seen by comparing the resistances of external (1/hA) and internal (L/kA) heat transfer where “A” is the transfer area in m^2 and “L” is the thickness of the wood board. For heat treatment conditions, the average values for jack pine are h=10 W/m^2.K, k=0.13 W/m.K, and L=0.0508 m (2 in) [Osma et al., 2008], and the ratio of internal to external heat transfer resistance is about 4. Therefore, if the gas is very hot, the surface of wood is exposed to high temperature for a longer time than the interior part which can result in non homogeneous properties.

For mass transfer, first the moisture has to be transferred from the interior of the wood to the surface. The wood diffusivities (see Equation 2) are a function of wood type, temperature, and the moisture content of wood similar to the other wood properties [Siau, 2006; Younsi et al., 2006]. Then, the moisture is transferred from the wood surface to the hot gas. If gas is too humid, then the moisture gradient between the gas and the wood surface is very small; thus, it will take a long time to eliminate the moisture (see equation 4). If gas is too dry, then the moisture transfer is very fast. This can result in mechanical defects. The fast moisture removal results in drier outer layers (shell) compared to the interior (core) part. In such a condition, the core prevents the shrinking of the shell. Consequently, the shell is in tension and the core is in compression. Surface cracks and checks may form due to the stretching of shell beyond the elastic limit. Later when the core starts drying, the shell which is already stretched can prevent the shrinking of the core. This time core goes into tension and the shell is in compression which may lead to internal cracks [Dietenberger, 1999; McCabe et. al., 1985]. Also, the moisture in gas is required for the thermal transformation reactions. The presence of moisture prevents the oxidation of wood [Ross, 2005]. This in turn affects the final properties of heat-treated wood.

As it can be seen from the above discussion, recipe adaptation and development require choosing suitable treatment conditions such as gas moisture content and heating rate which will yield a heat-treated wood product with desired properties and minimum mechanical property loss. In addition, the treatment conditions depend on the initial moisture content of wood and type of wood species to be treated.

METHODOLOGY

The research infrastructure of UQAC is shown in Figure 1. At UQAC, there are three furnaces available for research. First, the experiments are carried out in a laboratory scale thermogravimetric analyser. With this system, the treatment conditions can be changed easily. The experiments are carried out under different conditions and the heat-treated wood is characterized by carrying out bending (MOE, MOR), hardness, dimensional stability, and fungi tests depending on the desired final product properties. Once the promising conditions are identified, the treatment tests are carried out in the prototype furnace of UQAC followed by industrial furnace trials.

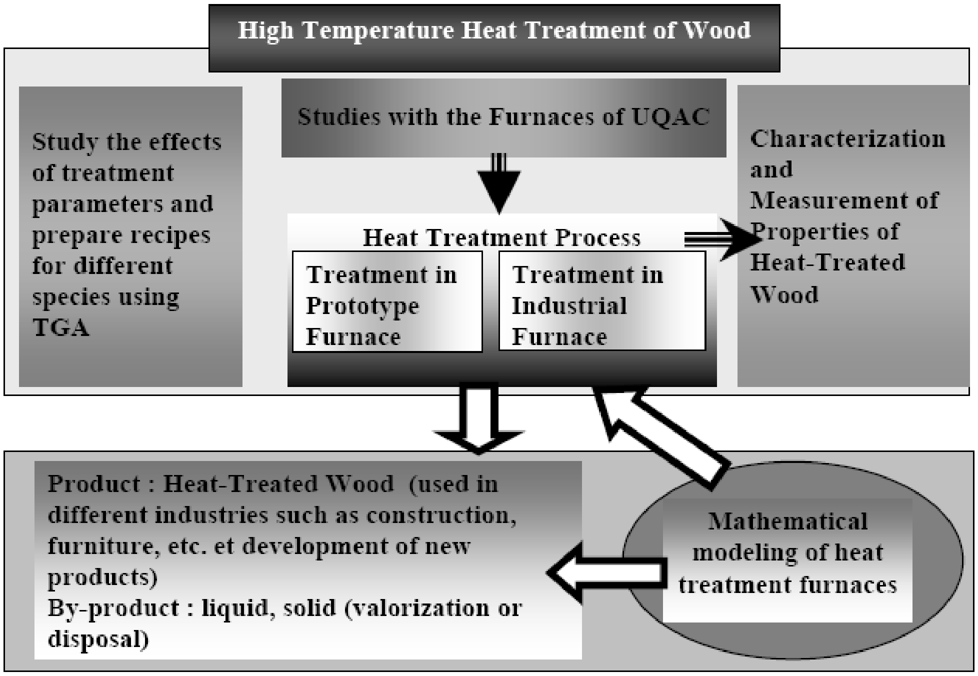

Figure 1. Research Infrastructure at UQAC.

Heat-Treatment Furnaces

Thermogravimetric analyzer is shown in Figure 2. The wood samples (0.035m x 0.035m x 0.20m) are suspended into a small electrical furnace from an electronic balance. Either the temperature profile or the change of mass of the sample can be measured during an experiment.

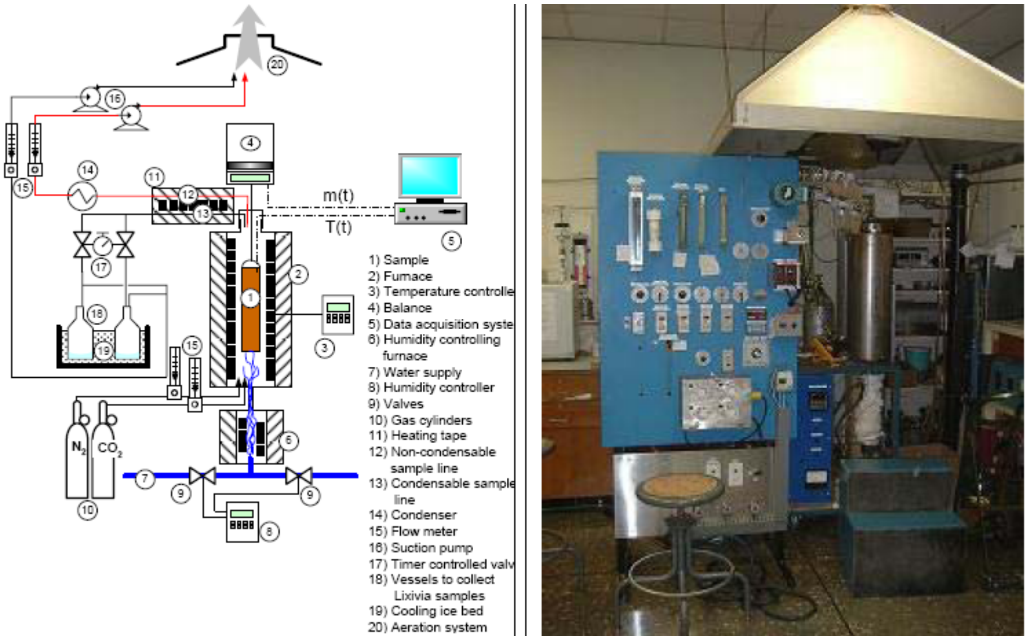

Figure 2. Thermogravimetric Analyzer.

Several thermocouples are placed into the sample in order to measure the temperatures at different positions within the sample. The positions of thermocouples are shown in Figure 3.

Another thermocouple is placed just under the sample to follow the gas temperature in the vicinity of the sample.

The data are collected with a data acquisition system. Since the presence of thermocouples alter the weight change data, two different tests (one with thermocouples to measure the temperature distribution, the other without thermocouples to measure the weight loss) are carried out under same conditions in order to have both mass loss and temperature profile history. Any treatment parameter can be changed easily in this system such as maximum treatment temperature, heating rate, treatment time, gas humidity, gas composition, etc. The condensables in the outlet gas is cleaned and discarded. In this system, it is also possible to analyze the gas or the lixiviate at different temperature intervals. Details of the system are reported elsewhere [Kocaefe et. al, 2007a].

The prototype furnace is shown in Figure 3a. This furnace is designed and built at UQAC. There is a patent in progress. In this system, a number of wood boards with standard dimensions can be treated. Figure 3b shows the industrial furnace. Due to confidentiality, the design details of these furnaces can not be given. The industrial trials can be carried out either at UQAC or at the plants of industrial partners.

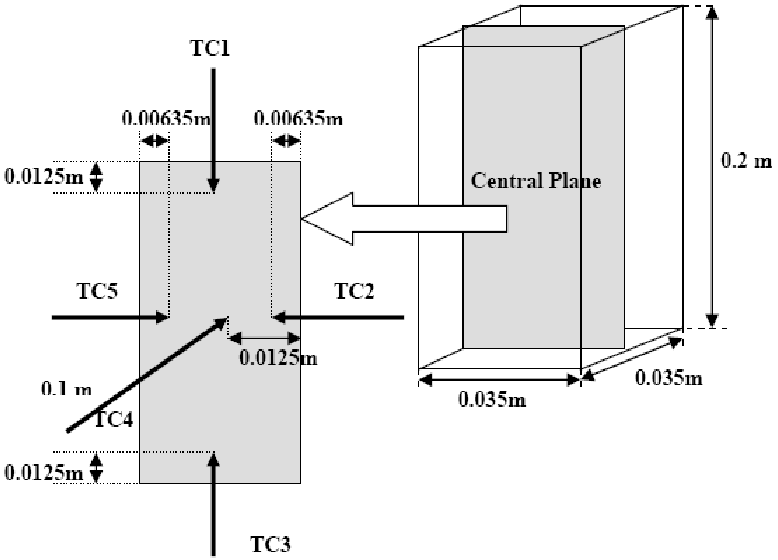

Figure 3. Positions of Thermocouples.

Characterisation Tests

These tests are explained in more detail in another section of this book as well as in other publications [Poncsak et al., 2006; Kocaefe et. al, 2008a]. The three point bending test is carried out according to ASTM D-143 standard using MTS Alliance RT 100 Universal Mechanical Test Machine. This standard requires sample dimensions of 0.0025cm x 0.0025 cm x 0.41 m. This is respected for the samples treated in the prototype and industrial furnaces. However, the wood dimensions of the samples treated in the thermogravimetric analyzer are smaller than the dimensions indicated by the ASTM standards. Therefore, the sample sizes were adapted for the bending tests (1cm x 1cm x 20cm) [Paulet and Bouazara, 2004]. The results of the thermogravimetric tests indicate the tendencies. This is important for investigating and comparing the effects of treatment parameters on the mechanical properties.

(a) (b)

Figure 4. (a) Prototype Furnace of UQAC; (b) Industrial Furnace of UQAC.

From the bending tests, the modulus of elasticity (MOE) and the modulus of rupture (MOR) are determined. The hardness, the dimensional stability tests, the screw withdrawal tests, and the mold resistance are conducted using ASTM D-1324-83, ASTM D 1037-105, ASTM D-1761-88, D3273-94 standards, respectively.

RESULTS AND DISCUSSIONS

Thermogravimetric Analysis

The treatment in this system is the first step of recipe adaptation or development. Figure 5 shows the North American jack pine samples treated using the thermogravimetric system.

Figure 5. Wood Samples Treated using the Thermogravimetric System at Different Temperatures.

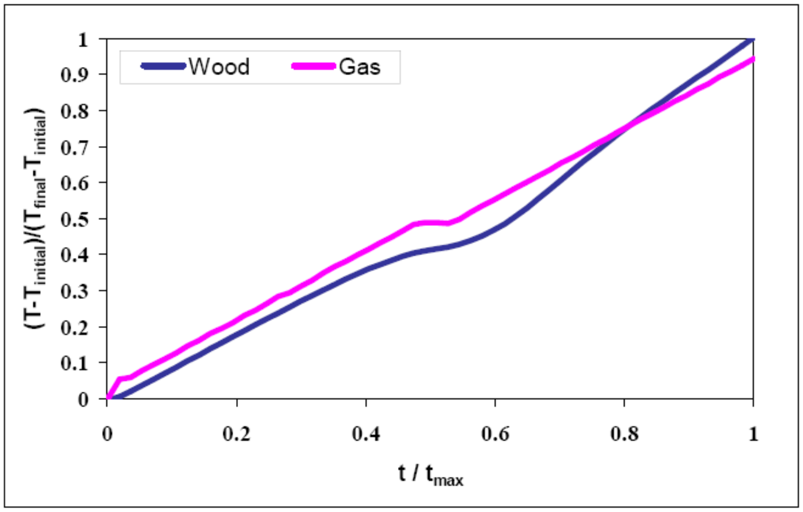

Figure 6. Comparison of Gas and Wood Temperatures During Heat Treatment for Species 1.

The temperatures measured at different positions of the sample are very similar. This temperature uniformity is very important for the wood characterization tests. Therefore, the temperature measured at the center of the sample will be used as the wood temperature here. The wood and gas temperature profiles obtained during heat treatment are compared in Figure 6. Since the wood is heated with the hot gas, the gas temperature is higher compared to that of the wood up to the temperature where the exothermic wood modification reactions take place. After this point, depending on the composition of the species studied, the wood temperature might exceed the temperature of the gas.

In this system, the effect of any heat treatment parameter can be studied. Figure 7 presents the effect of heating rate on the relative weight loss (Weight loss at time "t" / Total weight loss) of two different species. Since the maximum heat treatment time (t_{max}) is different for each heating rate, the t_{max} of the experiments carried out using 20°C/h of heating rate are used to normalize the data presented in this figure. As it can be seen, increasing the heating rate decreases the treatment time. The trend is similar for the species even if the decrease is quantitatively different. Increasing the treatment time exposes wood to high temperatures for a longer period of time. This in turn affects the properties of the heat-treated wood. However, if it is heated too fast, the treatment may not be uniform and can cause crack formation. Therefore, weight loss results should be analyzed in conjunction with the characterization results.

The effect of gas moisture content is shown in Figure 8. For species 2 the weight loss is higher when the moisture content of the gas is lower which results in high moisture gradient between the surface and the gas. However, for species 1 the reverse trend is observed. For some species when the gradient is very high, the initial moisture transfer is very fast.

Therefore, a thin surface layer dries rapidly forming a crust on the surface due to shrinking and hardening which in turn slows down further moisture transfer [McCabe et al., 1985; Rowel et al., 2000; Kocaefe et al, 2007a].

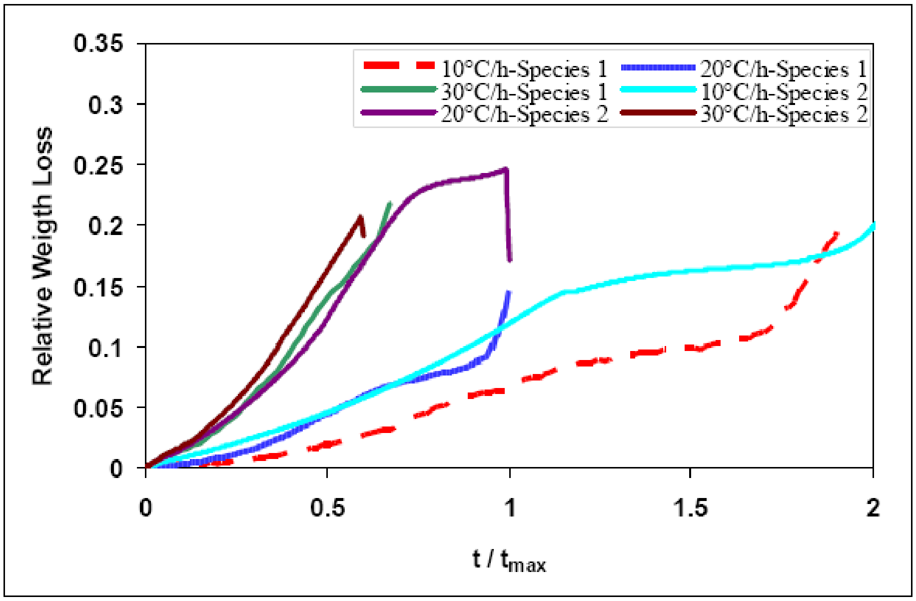

Figure 7. Effect of Heating Rate on Relative Weight Loss.

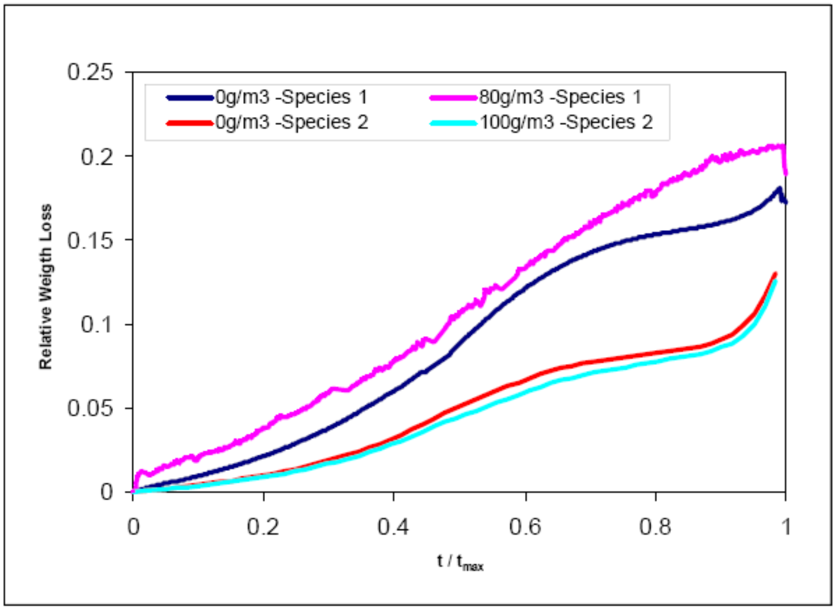

Figure 8. Effect of Gas Moisture Content on Relative Weight Loss.

After heat treatment, the characterisation tests are carried out. Some examples of these tests can be seen below. The effect of temperature and the heating rate on MOR are presented in Figures 9 and 10, respectively, for two species. It is observed that MOR stays relatively stable up to a certain temperature. After thermal modification reactions start, MOR decreases with temperature. MOR increases with increasing heating rate for these species. When the heating rate is high, the treatment time is short. Therefore, the mechanical properties are affected to a lesser extent. MOE does not seem to be affected by temperature (see Figure 11)

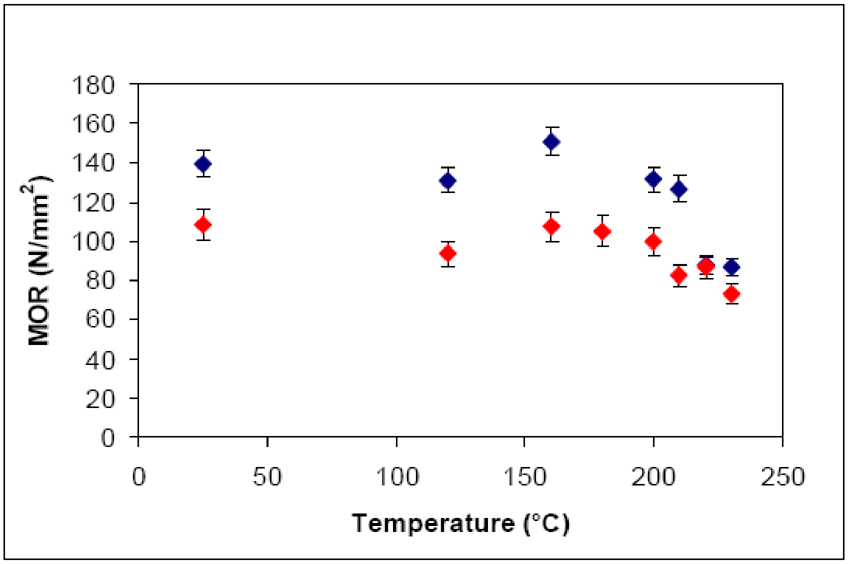

Figure 9. Effect of Temperature on MOR.

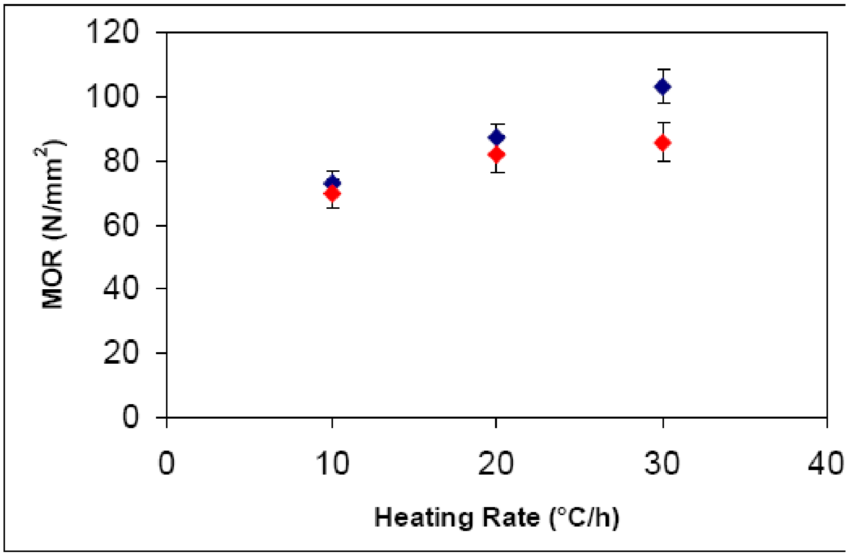

Figure 10. Effect of Heating Rate on MOR for Species 1 and 2.

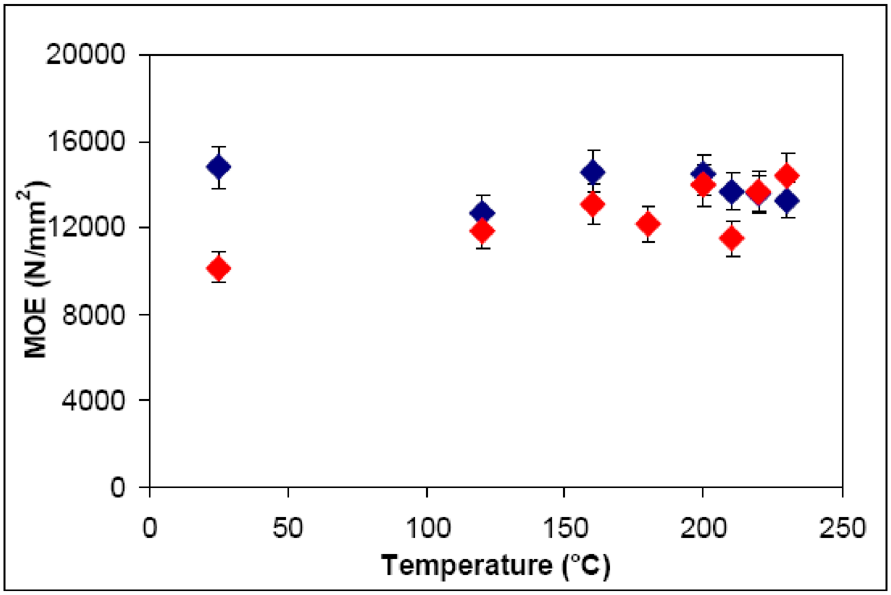

Figure 11. Effect of Temperature on MOE.

Figure 12 shows that the screw withdrawal resistance also starts to decrease for species 1 after the thermotransformation reactions start. Increasing heating rate seems to improve the screw withdrawal resistance (see Figure 13). This is in agreement with MOR data. From these results, it is clear that the temperature of treatment should not exceed 200°C to avoid significant reduction in mechanical properties for these two species. Figure 14 shows that the species 3 is most dimensionally stable at 220°C, and its hardness decreases during heat treatment.

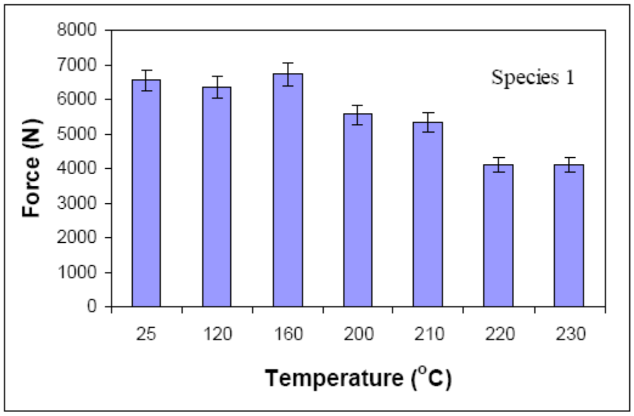

Figure 12. Effect of Temperature on Screw Withdrawal Resistance.

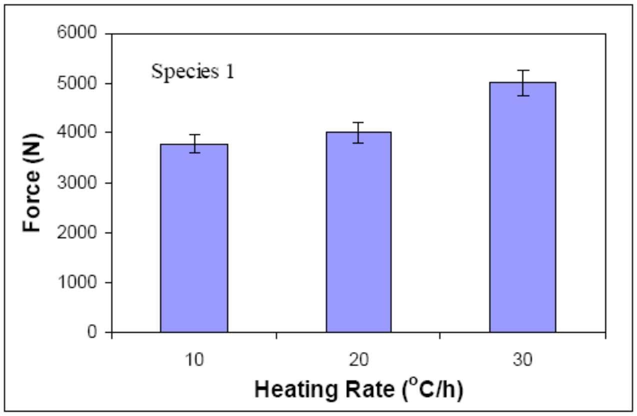

Figure 13. Effect of Heating Rate on Screw Withdrawal Resistance.

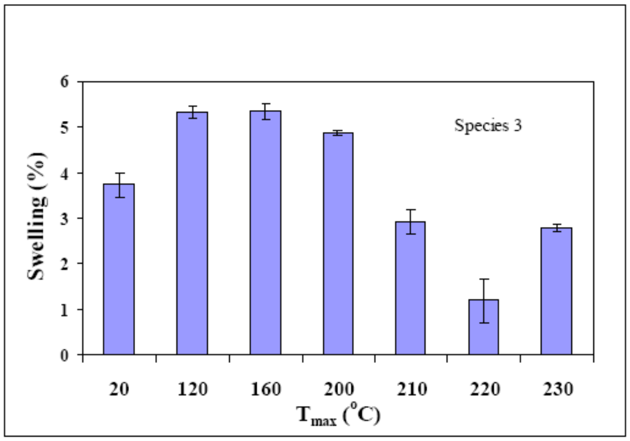

Figure 14. Effect of Heat Treatment on the Dimensional Stability in Radial Direction for Species 3.

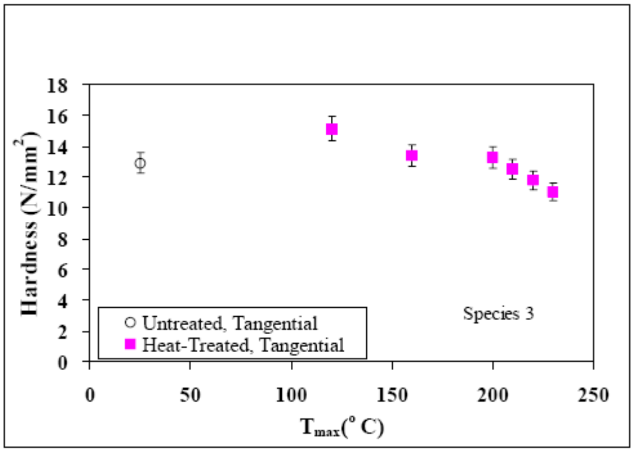

Figure 15. Effect of Heat Treatment on the Hardness for Species 3 in Tangential Direction.

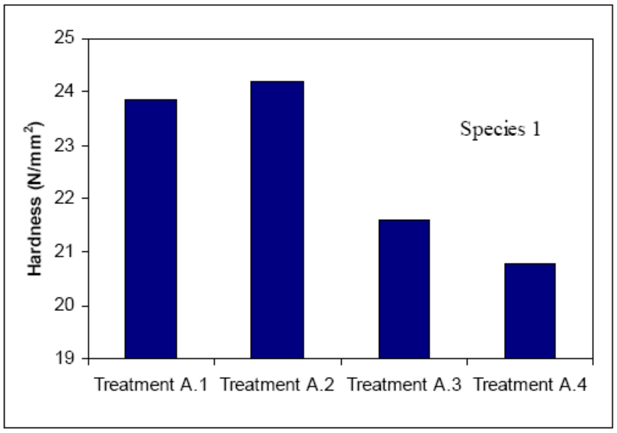

Figure 16. Hardness Tests During Recipe Development.

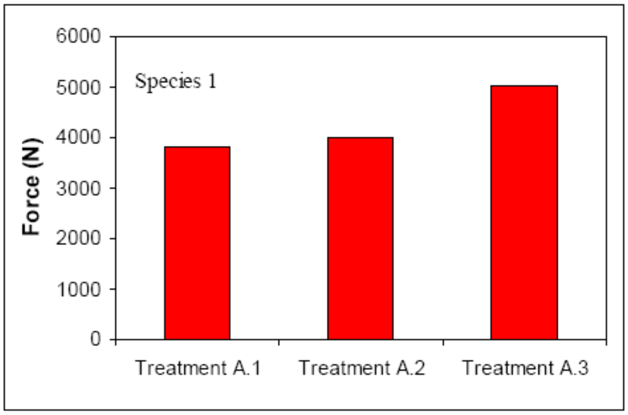

Figure 17. Screw Withdrawal Tests During Recipe Development.

It is also possible that the industry may want to improve a certain property of a wood species via heat treatment. In these cases, the heat treatment conditions are changed until the desired property is obtained. Figures 16 and 17 are examples of this method. The desired property might first improve, then it may again decrease, stay constant or may continue to improve.

Prototype Furnace and Industrial Trials

Once the tendencies are determined, chosen conditions can be tested in the prototype furnace. If the results are satisfactory, the recipe is tried under industrial conditions. The experience showed that the recipe developed in the thermogravimetric analyzer is successfully applicable in prototype and industrial furnace treatments. Figure 18 compares MOR of species 3 measured after treatment in laboratory, prototype, and industrial furnaces [Krause and Letourneau, 2005; Kocaefe et al., 2009]. Although the results of thermogravimetry are different than those of the prototype and the industrial furnace, it gives the right trends.

The difference can be explained with the significant difference in sample sizes used for the heat treatment and the bending test. The results of the prototype and industrial furnace tests are very similar.

The effect of heat treatment carried out in an industrial furnace on mold growth is shown in Figure 19. On the mold scale, 0,1,2,3,4, and 5 correspond to no mold growth, 5% or less, 6%-25%, 26%-50%, 51%-75%, and 76% or more mold coverage, respectively. The treatment affects different species differently. The mold resistance of species 1 was improved more compared to that of the species 3.

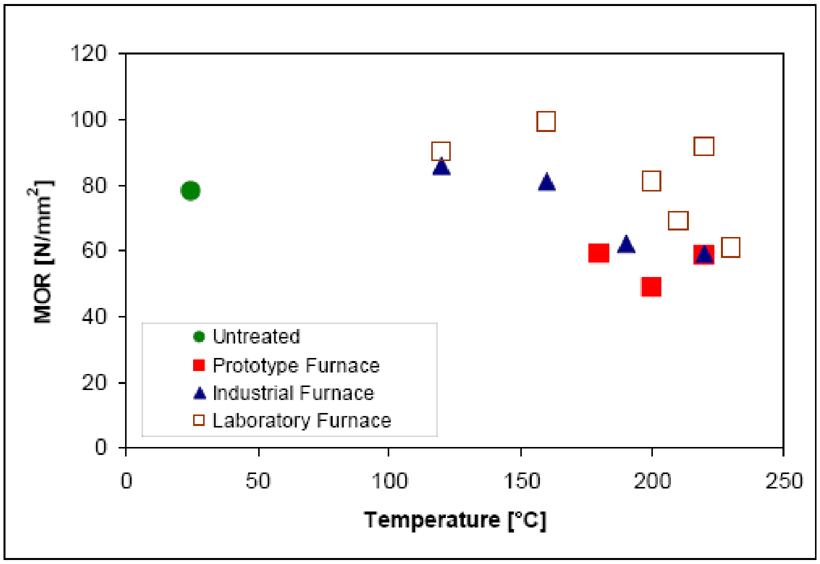

Figure 18. Comparison of MOR for Heat-Treated Wood in Different Furnaces.

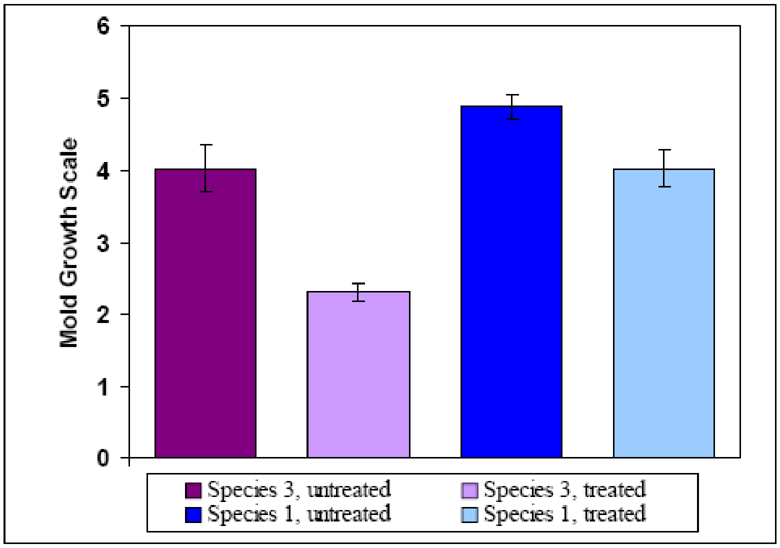

Figure 19. Comparison of Mold Growth for Species 1 and 3.

CONCLUSIONS

The method elaborated for the recipe adaptation and development works well. With this method, the heat treatment recipes developed for European species are adapted to North American species and new recipes are developed for various Canadian and American species in collaboration with industry.

First, small samples are treated under a wide range of conditions, and corresponding wood properties are measured. Then, the tests are carried out in the prototype furnace using standard size wood boards followed by industrial trials. The method makes the development of a heat treatment recipe possible for a specific application of a given species. If, for example, the application requires an improvement of 50% in one of the wood properties such as dimensional stability, the treatment conditions are sought to achieve this target. With the available infrastructure, any recipe can be developed easily.

Selection of the treatment conditions requires a comprehensive knowledge of heat and mass transfer mechanisms. The temperature and moisture gradients between the wood surface and gas play an important role in defining the heat treatment parameters and, consequently, the final properties of the value added wood product. One has to keep in mind that wood is an insulating material with low thermal conductivity. Therefore, fast heating rates create large gradients between wood surface and its interior leading to fast moisture movement and evaporation and resulting in non-uniform treatment of wood and mechanical property loss.

Mathematical modelling is another helpful tool for recipe development. With the model, conditions leading to uniform treatment can be identified. Different models developed are also used for improving the furnace design.

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