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Physical Properties and Drying Behavior of Hydrothermally Treated Yellow-Poplar

Sohrab Rahimi

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Physical Properties and Drying Behavior of Hydrothermally Treated Yellow-Poplar

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**Thesis submitted
to Davis College of Agriculture, Natural Resources and Design
at West Virginia University**

in partial fulfillment of the requirements for the degree of

**Master of Science in
Forestry**

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2017

**Key words: Physical Characteristics, Drying Behavior, Mechanical Properties,
Hydrothermal Treatment, Yellow-Poplar**

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Abstract

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Sohrab Rahimi

Non-chemical treatments (steam and ultrasonic vibrations) have been intensively researched and commercialized to make chemical-free wood products with enhanced mechanical properties and decay resistance; however, utilization of high-pressure steam medium involves vapor-phase reactions using high-temperature steam generated at the expense of high energy input. In this research, drying behavior, mechanical properties, and physical characteristics of wood (yellow-poplar) were compared to evaluate influence of reaction media (steam and hot-compressed water) and temperatures (100°C and 140°C). The control (no treatment) was used for reference comparison. For experiments, green samples of yellow-poplar heartwood were used for treatment. The average size of length (longitudinal direction), width (radial direction), and thickness (tangential direction) of the specimens were 22.53, 17.18, and 16.72 mm, respectively. After the treatment, the samples were dried under isothermal temperature condition of 105°C under nitrogen atmosphere to minimize the influence of humidity. Data from drying experiments were used to prepare drying curves, which were fitted with unsteady state molecular transport equation to calculate overall liquid diffusion coefficients. Dimensions, weight, and true volume (excluding pores) of samples were measured for green, treated, and dried samples and this data was used to calculate selected physical characteristics (moisture content, volumetric shrinkage, specific gravity, and total porosity). The dried samples were evaluated for water absorption, volumetric

swelling, modulus of elasticity, and compression strength. Statistical analysis of experimental data showed that the reaction media had significantly influenced moisture content, total porosity, diffusion coefficient, and compression strength. Intensified hot-compressed water treated and control samples had the most and least moisture contents (101.10% and 43.56%), respectively. In addition, wet and oven-dry specific gravity of the samples were in range of 0.42 to 0.44 and 0.49 to 0.50, respectively. Additionally, Intensified steam treated and control samples had the most and least total porosity (94.94% and 82.36%), respectively. Furthermore, mild hot-compressed water treated samples showed the greatest compression strength (47.75 MPa). Overall liquid diffusion coefficient of the untreated yellow-poplar was $3.15 \times 10^{-8} \text{ m}^2/\text{s}$. Except steam treatment at 140°C, other treatments significantly decreased diffusion coefficient.

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Table of Content

Abstract	ii
Acknowledgment	iv
Table of Content.....	v
List of Figures	vii
List of Tables	ix
Chapter 1. Introduction and Background Knowledge	1
1.1. Problems Related to Wood Drying	1
1.2. Various Physical Treatments Performed on Wood	2
1.3. Hydrothermal Treatments	3
1.4. Effect of Hydrothermal Treatments on Physical Properties and Drying behavior.....	7
1.5. Effect of Hydrothermal Treatments on Anatomical Structure.....	12
1.6. Effect of Hydrothermal Treatments on Mechanical Properties	16
1.7. Effect of Hydrothermal Treatments on Drying Behavior and Diffusion Coefficient.....	16
1.8. Effect of Hydrothermal Treatments on Chemical Make-up.....	18
1.9. Synthesis of Literature Review and Objective	19
Chapter 2. Material and Methods	20
2.1. Selection of Wood Species	20
2.2. Procurement of Raw Material and Processing	20
2.3. Measurements	23
2.4. Hot Compressed Water and Steam Treatment	23
2.5. Drying Experiment.....	26
2.6. Moisture Sorption Testing	26
2.7. Mechanical Properties Measurements.....	26
2.8. Yield (Y).....	27
2.9. Physical Characteristics and Mechanical Properties	28
2.10. Drying Behavior	32
2.11. Statistical Analysis.....	34

Chapter 3. Results and Discussion	36
3.1. Determination of the Maturity of Wood Samples.....	36
3.2. Physical Characteristics.....	39
3.3. Mechanical Properties.....	52
3.4. Drying Behavior and Overall Liquid Diffusion Coefficient.....	54
Chapter 4. Conclusion and Summary	61
Nomenclature.....	63
References.....	65

List of Figures

Figure 1. Steam treatment process.....	4
Figure 2. Steam explosion treatment process.....	5
Figure 3. Micro explosion processing equipment.....	6
Figure 4. The working states of micro explosion device.....	6
Figure 5. Hot compressed water process.....	7
Figure 6. Distribution of macro, micro, and mesospores for selected softwoods.....	11
Figure 7. Cross-section view of untreated birch.....	12
Figure 8. Cross-section view of treated birch at 140°C.....	13
Figure 9. Cross-section view of treated birch at 160°C.....	13
Figure 10. Cross-section view of treated birch at 180°C.....	14
Figure 11. Ray parenchyma cells and earlywood tracheids of an untreated fir.....	14
Figure 12. Collapses on pit membranes (a) and splits between pit borders and tracheid walls (b) in fir wood treated at 130°C and with 20 cycles.....	15
Figure 13. Splits in cross field pits of ray parenchyma cells and latewood tracheids (a) and damages on tracheid walls (b) in fir treated at 160°C with 10 cycles.....	15
Figure 14. (a) Cutting pattern of the discs from a log (b) cutting pattern of the cubic samples from a disc.....	21
Figure 15. Yellow-poplar control samples (upper left) and HCW treated samples in 100°C (upper right), 140°C (lower left), and 160°C (upper right).....	23
Figure 16. temperature and pressure as a function of time over the period of hydrothermal treatment.....	24
Figure 17. Experimental set-up for hydrothermal experiments	25
Figure 18. Instron machine for compression test.....	27
Figure 19. MC (dry-basis) (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	40
Figure 20. Volumetric shrinkage (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	43
Figure 21. Green specific gravity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	44

Figure 22. Oven-dry specific gravity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	45
Figure 23. Total porosity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	47
Figure 24. Water absorption (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	49
Figure 25. Volumetric swelling (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	50
Figure 26. Modulus of elasticity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	52
Figure 27. Compression strength (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	53
Figure 28. Moisture ratio as a function of time elapsed during drying at 105°C for untreated and hydrothermally treated samples of yellow-poplar.....	55
Figure 29. Drying rate as a function of moisture ratio for untreated and hydrothermally treated samples of yellow-poplar.....	57
Figure 30. Overall liquid diffusion coefficient (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	59

List of Tables

Table 1. Frequency of juvenile wood in different replications.....	36
Table 2. MC (dry basis) and volumetric shrinkage (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	39
Table 3. Green specific gravity and oven-dry specific gravity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	43
Table 4. Total porosity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	46
Table 5. Water absorption and volumetric swelling (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	48
Table 6. Modulus of elasticity and compression strength (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	52
Table 7. Drying time (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar to reach zero MC.....	56
Table 8. Overall liquid diffusion coefficient (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.....	59

Chapter 1. Introduction and Background Knowledge

1.1. Problems Related to Wood Drying

Wood drying consumes about 40% to 70% of the total energy consumed in wood manufacturing (Zhang and Liu, 2006). For this reason, much effort has been made on fast drying method with high drying quality. Vacuum drying is a good example, which can achieve drying rates 3 to 17 times faster than conventional drying (Ressel, 1994; Harris and Taras, 1984). Beside improvement of drying process itself, numerous studies have been devoted to treat wood prior to drying in order to enhance drying quality. Of all various modification processes, thermal treatment is by far the most commercially advanced that has long been known as a prospective effective method to boost dimensional consistency, improve decay resistance (Hill, 2006), and improve permeability by destroying pore blockage caused by tylosis in wood.

Tylosis is observed in several hardwood species, such as, white oak, black locust, and American black walnut due to accumulation of deposits and extractives during transition from sapwood to heartwood (Hoadley, 1990; Hoadley, 1980). Tylosis is an undesirable phenomenon, which reduces permeability and diffusion coefficient and consequently drying rate, by blocking the pathway of liquid water and vapor to move through wood medium. Several pretreatments have been offered to solve this issue. Alexiou et al. (1990) did pre-steaming treatment on eucalyptus heartwood before conventional drying and observed that it increased drying rate by 7-16%. In addition, volumetric shrinkage was not changed by pre-steaming. Dashti et al. (2012a) did microwave treatment on aleppe oak and observed distortion of the tylosis structure in the heartwood, resulting in a considerable climb in the air permeability. He et al. (2014) reported that ultrasound treatment prior to vacuum drying increased drying rate by opening the bordered pits and reducing the amount of extractives on the inner wood pores.

Like tylosis, wet pockets (wetwood) is a growth defect frequently observed in some wood species like sub-alpine fir (about 40% of fir boards). Wetwood is of high MC and concentration of bacteria, showing different physical, chemical, and biological properties than normal wood. Fir lumber containing wet pocket is very difficult to dry, creating highly stressed lumber with wide variations in final moisture content (MC) (Hartley et al., 1997). In addition, more extractives (Bourchier, 1967 and Haygreen and Wang, 1966) and more aspirated and encrusted pit membranes on tracheid cell walls (Bauch, 1973 and Wilcox and Schlink, 1971) were observed in wetwood than normal wood. Steam explosion treatment had been applied to Japanese cedar (Kanagawa et al., 1992) and subalpine fir (Zhang and Cai, 2006) to mitigate wetwood related issues. Treated samples showed more uniform final MC than untreated samples after drying using conventional kiln (Cai, 2006).

Another factor which affects drying is presence of false heartwood. Red heartwood or false heartwood is a growth defect frequently occurs in beech trees. The reason of its occurrence is not clear. Presence of false heartwood decreases drying rate, increases shrinkage, and possibility of drying defects such as casehardening (Shahverdi et al., 2013). Steaming or specific drying schedules have been recommended as a remedy to mitigate issues related to false heart issue (Trenciansky and Hansmann, 2007).

1.2. Various Physical Treatments Performed on Wood

To improve physical properties (water absorption, dimensional stability, permeability and diffusivity, and mechanical strength) and decay resistance of wood, several treatments, for example, high-pressure steam (Dashti et al., 2012 a; Dashti et al., 2012 b; Sayar and Tarmian, 2013; and Peng et al., 2012), steam explosion (Zhang and Cai, 2006), ultrasonic treatment (He et al., 2013 and He et al., 2014), heat treatment (Rousset et al., 2011) have been reported.

Another physical treatment involves use of ultrasound technology. Ultrasound technology is based on mechanical waves at a frequency beyond the threshold of human hearing, which is above 20 KHz (Chandrapala et al., 2013). In order to perform ultrasonic treatment, the material (wood) needs to be submerged in liquid medium such as water (Fernandes et al., 2008). Wood undergoes rapid succession of alternate compression and tension. Besides, ultrasound wave can create microcrack and very tiny cavitation, which might help eliminate strongly attached moisture from wood substance (Wan, 1992). He et al. (2013) performed ultrasonic treatment to improve quality of Chinese catalpa during vacuum drying. They reported that the ultrasonically treated (0.05) samples took only 41 h to dry from 99% to 11% of MC, compared to 52 h for the control specimens. Diffusion coefficients of the ultrasound treated samples at 0.05 MPa were 2.91×10^{-8} and $1.12 \times 10^{-8} \text{ m}^2.\text{s}^{-1}$ beyond and below the FSP, respectively. The diffusion coefficients of the control samples were lesser than those of treated ones whether below or above FSP.

More recently, renewed interest has been found in heat treatment processes to improve wood quality due to growing demand for sustainable building materials and due to regulations diminishing the application of toxic chemicals. Some of the commercial heat treatments are following: thermowood (Finland), platoWood (Netherland), OHT-oil treatment (Germany), bois perdure (France), and rectification (France) (Esteves and Pereira, 2009). The typical range of the temperature for heat treatment of wood is from 160°C to 260°C in presence or absence of moisture. In some methods, a shielding gas like Nitrogen is applied to remove or minimize the effect of relative humidity (Militz, 2002).

1.3. Hydrothermal Treatments

Several researches were focused on heat treatment in presence of steam or water, also referred as hydrothermal treatments. Different types of hydrothermal treatment were applied to improve wood

quality and drying process and consequently reduce energy consumption. Following are some examples: steam treatment (Peng et al., 2012; Sayar and Tarmian, 2013; Alexiou et al., 1990; and Dashti et al. (2012a), steam explosion (Cai, 2006 and Kanagawa, 1992), and micro-explosion (Ma et al., 2015).

1.3.1. Steam Treatment

Steam treatment is done in a laboratory steaming vessel equipped with heat and pressure indicators. Wood samples are placed inside the vessel and steam is injected into the vessel to reach desired temperature and pressure conditions. Samples are exposed to steam with desired temperature and pressure and kept inside the chamber for certain time (Peng et al., 2012) (Figure 1). After holding time, steam is gradually released.

Figure 1. Steam treatment process.

1.3.2. Steam Explosion Treatment

Steam explosion treatment is another technique used to improve drying quality (Zhang and Cai, 2006; and Kanagawa, 1992). In this process, wood samples are placed in a chamber to be heated with steam, which builds up pressure inside the chamber. Once the temperature and pressure reach the desirable point, samples are kept inside the chamber for a certain period of time. Following the

holding time, steam is released very rapidly in few seconds. Then, the steam-releasing valve is closed again and treatment cycle is repeated several times (Cai, 2006). Repeated treatment cycles lead to rupture of cell walls, thereby increasing porosity and mass transfer rate (Figure 2)

Figure 2. Steam explosion treatment process.

1.3.3. Micro-Explosion Treatment

More recently, micro-explosion technique is applied prior to wood drying. This technique is similar to steam explosion but safer and more convenient. In this process, specimens are placed inside a hermetical chamber. Bursts of high-pressure, room temperature air is injected inside the chamber. The pressure of the chamber is monitored using a pressure gauge located at the crest of the chamber. Following a quiescent state, the burst of air is rapidly ejected in a fraction of a second. The treatment cycle is repeated for a specified number of times (Figure 3 and 4) (Ma et al., 2016).

Figure 3. Micro explosion processing equipment (Ma et al., 2016).

Figure 4. The working states of micro-explosion device: 1) inlet port, 2) outlet port, 3) pressure gauge, 4) chamber, 5) piston, 6) rubber gasket, 7) wood, and 8) front-end cover (Ma et al., 2016).

1.3.4. Hot Compressed Water Treatment

For hot compressed water treatment, wood samples are placed in an autoclave, filled up with distilled water, or buffered hot water with pH of 7 or 8, and desirable holding time and temperature. Since the pH value of water medium changes during hydrothermal treatment, buffered hot water (pH 7 and 8) were used to keep pH of the medium constant over the period of hydrothermal treatment. Buffered hot water with pH equal to 7 comprised 411.75 ml $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$ (0.2 M) +

88.25 ml $C_6H_8O_7 \cdot H_2O$; and with pH equal to 8 comprised 483.25 ml $Na_2HPO_4 \cdot 2H_2O$ (0.2 M) + 13.75 $C_6H_8O_7 \cdot H_2O$ (Figure 5) (Taghiyari et al., 2011).

Figure 5. Hot compressed water process.

1.4. Effect of Hydrothermal Treatment on Physical Properties and Drying Behavior

Physical properties of wood have been classified into following six major categories: physical characteristics, mechanical properties, thermal properties, electrical properties, optical properties, and acoustical properties. The physical characteristics and mechanical properties are focus of current research.

Various types of hydrothermal treatments affect physical characteristics as well as mechanical properties and consequently drying behavior of wood. The influence of hydrothermal treatment on wood vary based on temperature, pressure, holding time, number of cycles, and medium.

1.4.1. Effect of Hydrothermal Treatments on Physical Characteristics

Physical characteristics of interest are moisture content, specific gravity, porosity, and shrinkage/swelling. It has been shown that steam treatment reduces MC of hardwoods. Peng et al. (2012) applied steam treatment on poplar at 100°C and 140°C and observed greater MC reduction

after steaming at 140°C than 100°C. They reported that steaming at 100°C mitigated MC of poplar boards of 2, 4, and 6 cm by 33.05%, 24.63%, and 23.00%, respectively; whereas, steaming at 140°C reduced MC of poplar boards of 2, 4, and 6 cm by 67.82%, 52.94%, and 78.27%, respectively. More reduction in MC took place when steaming was performed at 140°C than at 100°C because superheated steam at 140°C acted as a drying medium while at 100°C steam was effectively saturated and did not have the potential to gain extra moisture vapor. Similarly, Cai (2006) reported reduced MC after steam explosion treatment on subalpine fir in the temperature range of 120°C to 160°C.

Zhang and Cai (2006) reported that only reduction in MC takes place as results of steam treatment, post kiln drying results in wood products with uniform moisture distribution. For example, they reported that samples treated at 160°C and 2.6 bar had standard deviation of 4.6% for MC whereas it was 7.4% for untreated samples.

Most steam explosion treated samples resulted in better dryability and more uniform moisture distribution after drying them in conventional kiln using conservative and accelerated schedules. Standard deviation of final MC after conservative drying schedule for control samples was 7.4% while it improved for mild steam explosion treated samples (5.8%) and intensified steam explosion treated samples (4.6%). In addition, standard deviation of final MC for mild (5.4%) and intensified (3.8%) steam explosion treated samples followed by accelerated drying schedule were lower than that of control samples (7.4%) followed by accelerated drying schedule (Cai, 2006). Peng et al. (2006) performed steam treatment for 2 h on poplar species with 20 mm thickness and reported reduced MC. Rate of reduction in MC for the samples treated at 100°C and 140°C were 16.53 and 33.91 %/h.

Hydrothermal treatment also affects dimensional stability. For example, steam explosion treatment at 160°C (6.2 bars of pressure) followed by conservative drying schedule has shown thickness shrinkage and width shrinkage of 3.85% and 3.92%, respectively, which were significantly greater than thickness shrinkage (2.57%) and width shrinkage (2.73%) of control samples. Likewise, steam explosion treatment at 160°C (6.2 bars of pressure) followed by accelerated drying schedule has shown thickness shrinkage and width shrinkage of 4.14% and 3.27%, which in turn, were considerably greater the values of control samples. However, drying schedule (conservative and accelerated) did not show significant difference. Notwithstanding, milder treatments i.e. at 120°C (2 bars of pressure) and 130°C (2 bars of pressure) did not significantly change shrinkage values compared to control samples (Cai, 2006). Dundar et al. (2012) performed heat treatment at 180°C and 210° for 3 h on Black pine (*Pinus nigra* Arnold). After 48 h of water immersion, the volumetric swelling of the control samples reported 13.88%. Heat treatment at 180°C resulted in volumetric shrinkage of 9.96%, which was considerably lower than the value of control sample. In addition, heat treatment at 210°C showed pronouncedly considerable reduced volumetric shrinkage (7.81%).

Specific gravity or density is perhaps the most important feature in wood heat (hydrothermal) treatments which is affected mainly by loss of mass. Loss of mass, as a result of hydrothermal treatment depends on several factors such as wood species, heating medium, temperature, and treatment time (Esteves et al., 2009). Mazela et al. (2003) studied the mass loss of heat treated pine species (*Pinus sylvestris*) at 160°C, and 190°C, and 220°C during 6 and 24 h in presence and absence of vapor. They observed similar mass loss in different heating media after 6 h; however, after 24 h the mass losses in air is greater than in vapor especially at the temperatures of 190°C

and 220°C. Bourgois and Guyonnet (1988) claimed mass loss of maritime pine treated at 260°C was quite high, that was, 18.5% and 30% after treatment time of 15 and 60 min, respectively.

1.4.2. Effect of Hydrothermal Treatments on Pore Characteristics

Drying has remarkable impact on pore characteristics and consequently density and specific gravity of wood. Wood is a porous material with micropores, mesopores, and macropores present. The porosity of wood largely depends on the density and anatomy of the wood species. Typically, porosity or fractional pore volume of wood ranges from 54.29% to 80.41% for hardwoods having a green specific gravity in the range of 0.30 to 0.70 (Plotze and Niemz, 2011 and Siau, 1995). Compaction of bound water has been neglected in these calculations. Typically, wood has micropores (< 80 nm), mesopores ($500 - 80$ nm), and macropores (> 500 nm). The micropore volume varied from 1.6% to 4.8% for the 18 wood species tested (Weatherwax and Tarkow, 1968).

Plotze and Niemz, (2011) tested air dried samples of several ring porous, diffused porous, and softwoods for porosity and pore size distributions (Figure 6). On average, wood samples contain cumulative pore volume of $821 \text{ mm}^3/\text{g}$ and hardwoods had on average 60% of the pore volume of softwoods. While softwoods had low microporosity, the hardwoods showed varying combinations of all three types of pores; however, all the woods tested had mesopores below 50%. High pore volume was observed for white alder, common birch, and sycamore maple hardwoods due to the presence of macropores (79% to 90%) as well as for Gavoona and Opepe hardwoods due to the presence of micropores (about 80%). On average, the specific surface area for white alder, common birch, and sycamore maple hardwoods was $70 \text{ m}^2/\text{g}$ and total pore volume was $1173 \text{ mm}^3/\text{g}$.

Figure 6. Distribution of macro, micro, and mesopores for selected softwoods (Plotze and Niemz, 2011).

It has been shown that wood when dried from green to oven-dry shrinks and loses not only total porosity but also changes pore size distribution (Park et al., 2006). Park et al. (2006) reported that the fiber wall begins to collapse starting with larger pores (> 100 nm) followed by the sequential collapse of smaller pores (< 10 nm) as the moisture ratio drops below 0.8 g/g (g of water/g of dry wood) during drying. That is why the average pore diameter was 80 nm for moisture ratios above 0.8 g/g, which reduced to 20 nm when moisture ratio reached below 0.3 g/g. Further heat treating of oven-dry wood up to 200°C leads to decreased nano-pore shares due to further shrinkage of cell walls and flowing of lignin (glass transition temperature 165 - 170°C) in the cell-wall pores and resulting reduced micropore spaces. Additional heat treatment after drying also reduced the FSP for all the woods tested. For example, the FSP for spruce decreased from 38.0% to 25.8% due to

heat treatment at 200°C. Therefore, to get most use of wood porosity, wood treatments should be performed on green wood to improve its physical characteristics and decay resistance.

1.5. Effect of Hydrothermal Treatments on Anatomical Structure

Biziks et al. (2013) provided a pioneering study on how anatomical properties (growth rings, cell wall, lumens, and fibers) of birch wood change during hydrothermal treatment which showed that hydrothermal treatment at 180°C for 1 h can break up the integrity of wood morphological structure. The study reported the results of hydrothermal treatment of birch wood at 140°C, 160°C, and 180°C, under pressure of 5-9 bars. lumen sizes were least affected during treatment. The lumen cross-section decreased by 2.3%, while the tangential length of the lumen decreased by 0.5% and the radial length of the lumen decreased by 2.7%. In contrast, the cross-sectional area of the fibers decreased from 1.0% at 140°C and 20.7% at 180°C mainly due to degradation of cell wall constituents (Figure 7, 8, 9 , and 10).

Figure 7. Cross-section view of untreated birch (Biziks et al., 2013).

Figure 8. Cross-section view of treated birch at 140°C (Biziks et al., 2013).

Figure 9. Cross-section view of treated birch at 160°C (Biziks et al., 2013).

Figure 10. Cross-section view of treated birch at 180°C (Biziks et al., 2013).

While significant structural damage takes place at temperatures as high as 180°C, some minor fractures in bordered pit membrane have been noticed at temperature of 130°C, which steam explosion treatment was reported 20 times (Figures 11, 12, and 13) (Zhang and Cai, 2006).

Figure 11. Ray parenchyma cells and earlywood tracheids of a untreated fir (Zhang and Cai, 2006).

Figure 12. Collapses on pit membranes (a) and splits between pit borders and tracheid walls (b) in fir wood treated at 130°C with 20 explosion cycles (Zhang and Cai, 2006).

In fact, about 6% to 13% samples treated at 160°C through steam explosion collapsed during post-treatment kiln drying, which essentially indicated that the treatment significantly altered cell walls (Figure 13) (Zhang and Cai, 2006).

Figure 13. (a) Splits in cross-field pits of ray paranchyma and latewood tracheids (a) and damages on tracheid walls (b) in fir treated at 160°C with 10 cycles (Zhang and Cai, 2006).

1.6. Effect of Hydrothermal Treatments on Mechanical Properties

Mechanical properties of wood are principally divided into three groups including elastic properties, strength properties, and frictional properties. Hydrothermal treatments can influence mechanical properties of which modulus of elasticity (MOE) and modulus of rupture (MOR) are discussed here.

Steam explosion contributed to significant reduction in both MOE and MOR of wood samples. Cai (2006) reported that the MOE for the control samples was 8205 MPa, which reduced to 6619 MPa for samples, which were treated at 160°C. Likewise, the MOR reduced from 34.07 MPa to 18.89 MPa for the steam treatment.

In another research, Zhang and Cai (2006) reported that the MOE for control samples (fir) (conventional kiln drying) was 8205 MPa, which became which became 8274, 8067, 8136, and 6619 MPa for the samples treated at 120°C, 130°C, and 160°C

1.7. Effect of Hydrothermal Treatments on Drying Behavior and Diffusion Coefficient

Wood drying is considered as the costliest process in wood industry; hence, decrease in wood drying time as a mean to saving in energy consumption and consequently drying expenses, plays an incredible role in this industry (Zhang and Liu, 2006). It is also worth noting that minimization in drying time does not have to lead to wood quality reduction. Drying time is controlled by several factors, among which moisture diffusion coefficient is a key parameter (Dashti et al., 2012a). Diffusion coefficient proposes a functional way to estimate the drying time in the domain of bound water and final moisture profile in wood. Thus, it is possible to convert a moisture based drying schedule to a diffusion time schedule, which has been successfully applied for a number of softwood species (Tarmian et al., 2012).

Steam treatment from 120°C to 160°C has reportedly improved mass transfer properties, especially air permeability, of fir samples (Dashti et al., (2012b)). However, treatment at high temperature (200°C) mass diffusivity (property of mass migration under the effect of a concentration gradient) has been reported to reduce significantly due to chemical modification of cell wall (Rousset et al., 2004).

Perhaps, wood permeability influences surface moisture evaporation and internal moisture (Torgovniko and Vinden, 2009), which in turn control drying rates. Peng et al. (2009) compared drying rate of control, steam treated at 100°C, and steam treated at 140°C for poplar and Manchurian walnut. They reported that overall drying rates decreased linearly with reduction in MC; however, untreated samples dried faster than the treated ones. They reported that below 25% of MC, drying rates of untreated samples decreased faster than those of treated ones. In other words, below FSP, drying rates of treated samples had been higher than those of control samples for both species because of two reasons. First, there is not enough free water below FSP to block the capillary pores which render water vapor transport more rapidly. Second, steam treatments enhance gas permeability of wood by damaging bordered pits and aspirated pits (Lu et al., 1994). Therefore, total drying time of poplar boards (6 cm thickness) for untreated and treated at 140°C, were 102 h and 74 h, respectively. Likewise, steam explosion and microexplosion treatment has shown significant improvement in dryability of subalpine fir lumber because it breaks down the bordered pits among earlywood tracheids (Cai, 2006; Zhang and Cai, 2006; Ma et al., 2015 and Ma et al., 2016). Ma et al. (2016) treated poplar samples five times with pressure of 1.0 MPa followed by oven-drying at $103 \pm 2^\circ\text{C}$. Untreated samples were dried similarly to make comparisons. Results revealed that drying rate of treated samples was noticeably greater than that of control ones above FSP; whereas, drying rate of treated samples below FSP was increased

inconspicuously and even reduced for the specimens with MC of 70% and 30%. In general, increase of drying rate (above and below FSP) and effective water diffusion coefficient were discovered (Ma et al., 2015).

In another research, Sayar and Tarmian (2013) quantified calculated vapor diffusion coefficients. They performed 12 sets of steam treatment on poplar to investigate the effect of hydrothermal pretreatment on water vapor diffusion coefficient. Experiments were done at four different temperatures of 120°C, 140°C, 160°C, and 180°C and three different holding time of 1, 2, and 4 h. Diffusion coefficients were measured using Fick's law of diffusion in steady-state conditions. Results disclosed that increasing treatment temperature from 120°C to 140°C, 160°C, and 180°C did not significantly affect diffusion coefficients of the treated specimens. Likewise, increasing treatment time from 1 to 2, and from 2 to 3 h did not show significant influence on diffusion coefficients of the treated specimens. However, diffusion coefficients were in the range of 1.34×10^{-9} to $1.90 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ for control samples. The vapor diffusion coefficients for the steam treated samples were in the range of 0.14×10^{-9} to $0.59 \times 10^{-9} \text{ m}^2\text{s}^{-1}$. In a nutshell, resistance to water vapor diffusion significantly increased as results of steam treatment. Similarly, Ma et al. (2015) reported effective water diffusion of treated samples to be $4.75 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ and $0.8 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ for control samples.

1.8. Effect of Hydrothermal Treatments on Chemical Make-up

Hydrothermal treatment is performed under either steam medium or hot-compressed water medium. While steam treatment facilitates reactions in wood in vapor-phase, hot compressed water treatment under sub-critical conditions might change wood ultrastructure differently because it promotes reactions and mass transport in liquid-phase. Fourier transform infrared spectroscopy (FTIR) analysis of combined hydrothermal and dry heat treated wood showed that various

temperatures and media created different changes in wood components. (Tjeerdsma and Militz, 2005) analyzed beech and scots pine using FTIR to investigate chemical changes happened to wood components after two-step heat treatment including first moist condition at 165°C to 195°C in pH of 5.5 (adding sodium acetate solution) and secondly dry condition at 180°C (using continuous N₂ gas flow). Results showed acetyl groups were mostly found to be cleaved over high temperature treatment of the wood. In contrast, only partial deacetylation occurred at moderate treatment temperature. Esterification reactions, on the other hand, occurred in dry conditions at raised temperature. Esterification contributes in hygroscopicity reduction of wood and consequently enhanced durability and dimensional stability. Nonetheless, cross-linking reactions known to occur during thermal treatment plays more pivotal role than esterification in reduction of hygroscopicity.

1.9. Synthesis of literature Review and Objective

It is anticipated that hydrothermal treatment and steam treatment should have different effect on physical characteristics and drying behavior of wood because the former one facilitates wood reactions in liquid medium while the latter one promotes reactions in vapor medium. Liquid water and vapor move differently through wood medium. Liquid water movement is dominated by capillary (convective movement) while vapor water movement is dominated by diffusion, which is more random and less uniform (Siau, 199 and Siau, 1984). Therefore, objective of this research was to compare effect of hot-compressed water (HCW) and steam treatments at 100°C and 140°C on the selected physical characteristics, mechanical properties (modulus of elasticity and compressive strength) and drying behavior of yellow-poplar.

Chapter 2. Materials and Methods

2.1. Selection of Wood Species

Yellow-poplar (*Liriodendron tulifera*) was selected as test species because sufficient research data on its mechanical and physical properties is available in the literature and it is widely used by the wood industry (Wiemann, 2010). Yellow-Poplar is abundantly available in West Virginia and Appalachian forest. An investigation carried out on the number of species encountered on 30 active timber harvests in West Virginia by Grushecky et al. (2012). They reported that Yellow-poplar is the most prevalent timber harvested (25.5%) in West Virginia, followed by red maple (14.0%) and black/red oak (9.6%). In addition, this investigation considered number of prevalent species trees measured on 30 active timber harvest in West Virginia during 2008. According to the report, yellow-poplar is one of the most percentage of standing trees (25.5%) followed by white/chestnut oak (18.3%) and soft maple includes red maple (14.0%). Typically, 96.4% of a pine tree (wood volume) and 91.0% of a yellow-poplar tree (wood volume) are utilized.. Nevertheless, yellow-poplar is of 8th rank in terms of land utilization (97.6%), standing behind hard maple (99.4 %). On the other hand, the vast majority of yellow-poplar merchandized in West Virginia is devoted to sawlog (45.6%), peeler (26.2%), pulp (13.8%), rail (10.6%), and scragg (1.2%). Also, 2.6% of Yellow-poplar goes waste (Grushecky et al., 2012).

2.2. Procurement and Processing of Raw Material

Freshly cut log of Yellow-poplar (diameter = 175 ± 15 mm, length = 900 ± 20 mm) were procured from the West Virginia University (WVU) Research Forest. Immediately after procuring, ends of the logs were coated twice with paraffin and then kept inside a plastic bag to avoid moisture loss prior to the sample preparation.

Three discs with average thickness of 23 ± 1 mm were cut from a procured fresh log. In addition, the discs were cut from same place to avoid any possible variation, which might happen due to longitudinal variability through the log (Figure 14a).

In the next step, 115 small rectangular specimens were cut from the heartwood part of three discs, of which 78 samples were used for the experiments. Samples were prepared based on the cutting pattern represented in Figure 14b. All the samples were visually inspected for presence of wood closer to pith. Therefore, samples were divided into two groups. All samples, which come from proximity to the pith (about first 15 growth rings) were placed in the first group. Second group included the samples, which did not come from the zone close to the pith. Most of the samples (67 out of 78) come from the second group and the rest of the samples (11 out of 78) come from the first group.

Figure 14. (a) Cutting pattern of the discs from a log (b) cutting pattern of the cubic samples from a disc.

Typical dimensions of the samples were 17.18 mm radial, 16.72 mm tangential, and 22.53 mm longitudinal directions. There was a concern that 11 samples used from the first group might contain juvenile wood due to nearness to the pith, which could affect some physical and mechanical properties (Bowyer et al., 2007). Therefore, Shapiro-Wilk statistical test was performed to check normality of each replication having some of those 11 samples. Each replication had 6 samples for measurements. To make sure that those 11 samples were not come from juvenile wood, specific gravity of them was compared with the rest of the samples. specific gravity has been known as the most important criterion to discern juvenile wood from mature wood (Bowyer et al., 2007).

All the slicing and cube cutting operations for sample preparations were performed using a band-saw (Model: catalog number: 28-350, Rockwell, Pittsburgh, Pennsylvania,). The samples used for the experiment came from heartwood component of wood. Additionally, heartwood was chosen due to its richness in extractives, which was expected to redistribute during the hydrothermal treatment, making significant changes in physical characteristics and drying behavior (Hoadley, 1990; and Hoadley, 1980).

Total 78 rectangular blocks were cut and cleaned to remove any dust particles from its surface. Immediately after specimen preparation, they were held in deionized water to avoid loss of green moisture. To avoid microbial spoilage, distilled water was replaced at the interval of every 48 h prior to treatments. Six specimens were used as control. Other specimens were assigned random hydrothermal treatments, which were combination of following two treatment factors: Factor-1: medium (hot-compressed water or steam) and Factor-2: temperature (100°C and 140°C). Each experiment was replicated three times.

2.3. Measurements

Each sample was weighed with accuracy of 0.01 g using a weighing balance (Model: P603DMDS, Denver instrument, USA). True volume of the samples was measured using a pycnometer (Model: Manual Multipycnometer, Qunatachrome, FL, USA). This instrument measures true volume of substance (excluding pore volume) using fluid (nitrogen) displacement method. Length, width, and depth dimensions of cubical samples were measured using caliper (Model: ROHS NORM 2002/95/EC, Digimatic, Mitutoyo, Japan) with accuracy of 0.01 mm. Each dimension was recorded at three locations along a dimension to improve accuracy. Same sets of measurement were done three different times, i.e. prior to pretreatments, before drying treatment, and after drying treatment as well.

2.4. Hot Compressed Water and Steam Treatments

Combination of two treatment factors (medium and temperature) resulted in following four types of hydrothermal treatments: 1. Hot-compressed water (HCW) at 100°C (mild HCW), steam at 100°C (mild steam), HCW at 140°C (intensive HCW), and steam at 140°C (intensive steam). However, to determine the temperature for intensive treatment, several mock tests were performed earlier. Given the results of mock tests, 140°C was chosen because all the samples treated in HCW beyond 140°C (190°C, 170°C, and 150°C) became dark colored, brittle, and fragile (Figure 15).

Figure 15. Yellow-poplar control samples (upper left) and HCW treated samples in 100°C (upper right), 140°C (lower left), and 160°C (upper right).

All treatments were performed for a holding time of 1 h. During the treatment, temperature and pressure were recorded. Temperature and pressure as functions of time are represented in Figure 16.

Figure 16. Temperature and pressure as a function of time over the period of hydrothermal treatment.

Hydrothermal treatments were performed inside a one-liter sealed pressure reactor (Model: 4500, Parr Instrument Company, Moline, IL, USA). The schematic of the parr reactor is represented in Figure 17.

Figure 17. Experimental set-up (Singh and Sivanandan, 2014) for hydrothermal experiments.

For a typical HCW experiment, about six specimens were placed inside the pressure reactor. After that, distilled water was added to the reactor, approximately seven times of total six sample weight (Singh Seehra et al., 2015), to keep specimens submerged in water. The weight of the reactor containing wood specimens and water was recorded before and after each experiment. After that, the reactor was sealed and heated up to desired temperature, which was held for 60 min for all experiments.

To perform treatments in the steam medium, a perforated plate was placed inside the reactor vessel just above water table and all the specimens were placed on the perforated plate without touching water. After the hydrothermal treatment was complete, the reactor was allowed to cool-down to room temperature.

After hydrothermal treatment, all the six specimens were taken out of the vessel and surfaces were wiped with a blotting paper. Weight, dimensions, and true volume were measured for the six specimens. After that, drying experiments were performed on these specimens.

2.5. Drying Experiment

Samples were dried in ThermoGravimetric Analyzer (TGA) (Model: LECO 701, LECO Corporation, St. Joseph, MI, USA) at isothermal temperature at 105°C. Drying process was done in nitrogen conditions to avoid the effect of humidity. During each drying experiment, data on time, temperature, and weight of the samples were continuously recorded in a computer. After the drying experiments, sample weight, dimensions, and true volume were measured again.

2.6. Moisture Sorption Testing

After drying experiment, the samples were immediately placed under water for 24 h and then the weight and dimensions were measured again to evaluate water absorption and volumetric swelling.

2.7. Mechanical Properties Measurement

Lastly, compression test was done using Intron (Model: 825 Digital Electronic Instron/MTS machine University Avenue, Norwood, and MTS 318 System Cop., MPLS, MN USA) to determine modulus of elasticity and compression strength of the samples following ASTM D143-14 (Figure 18). Prior to the mechanical test, the samples were placed inside the conditioning chamber at $20 \pm 2^\circ\text{C}$ and relative humidity of $65 \pm 5\%$ to reach target equilibrium moisture content (EMC) of 12%. Samples were weighed before and after putting in conditioning chamber to evaluate MC. Average MC of the specimens were 13.1%, which was close to meet the requirement of ASTM.

Figure 18. Instron machine for compression test.

2.8. Yield (Y)

In order to estimate mass loss of wood substance post treatment, yield of the experiment was calculated. The more yield is, the less mass loss should be. Yield was evaluated using equation (1) as given below:

$$Y = \frac{m_2(1 - \frac{MC_{w2}}{100})}{m_1(1 - \frac{MC_{w1}}{100})} \times 100 \quad (1)$$

Where:

Y= yield (%)

m_1 = weight of moist wood before treatment (g)

m_2 = weight of moist wood after treatment (g)

MC_{w1} = Wet-basis MC before treatment (g)

and MC_{w2} = Wet-basis MC after treatment (g)

MC_w was calculated by equation (2) as given below:

$$MC_w = \frac{m-m_0}{m} \times 100 \quad (2)$$

Where:

MC_w = wet-basis MC (%)

m = moist weight (g)

and m_0 = oven-dry weight (g).

2.9. Physical Characteristics and Mechanical Properties

2.9.1. Dry-basis Moisture Content (MC_d) and Volumetric Shrinkage (s)

Dry-basis moisture content (MC_d) of wood is the mass of moisture in wood expressed as a percentage of the oven-dry mass (Siau, 1995). Wood is dimensionally stable when the MC is beyond the fiber saturation point (FSP). However, its dimensions change when it gains or losses moisture below that point. It shrinks as losing moisture in the cell walls and swells when gaining moisture in the cell walls (Forest Products Laboratory, 1999).

MC_d was calculated using equation (3) as given below:

$$MC_d = \frac{m-m_0}{m_0} \times 100 \quad (3)$$

Where:

MC_d = dry-basis MC (%)

Volumetric shrinkage was calculated using equation (4) as given below:

$$s = \frac{V-V_0}{V} \times 100 \quad (4)$$

Where:

s = volumetric shrinkage (%)

V = wet volume of moist wood (cm³)

and V₀ = oven-dry volume of wood (after drying) (cm³).

2.9.2. Green and Oven-dry Specific Gravity (SG and SG₀)

The specific gravity of wood is the ratio of the oven-dry mass to the mass of water displaced by the specimen at a given MC (Siau, 1995). Specific gravity is a unitless number because it is a ratio of masses. It is clearly known that an increment in bound water content creates swelling that will decrease the specific gravity. The maximum value of specific gravity is under oven-dry conditions and the minimum value is above the FSP which is called basic specific gravity or green specific gravity. Green specific gravity (SG) and oven-dry specific gravity (SG₀) were calculated using equations (5 and 6), respectively as given below:

$$SG = \frac{m_0}{V \times \rho_{water}} \quad (5)$$

$$SG_0 = \frac{m_0}{V_0 \times \rho_{water}} \quad (6)$$

Where:

SG = green specific gravity at an MC

SG₀ = oven-dry specific gravity at zero MC

and ρ_{water} = density of water (g/cm³).

2.9.3. Total Porosity (μ_{total})

Porosity is fractional void volume of wood expressed in percentage at a given MC (Siau, 1995).

$$\mu_{total} = \frac{V-V_{p0}}{V} \times 100 \quad (7)$$

Where:

μ_{total} = total porosity (%), which is equal to fractional volume occupied by air plus water fraction in green condition.

V_{p0} = oven-dry true volume of wood cell mass (cm^3).

Total porosity can also be calculated by equation (8) as given below:

$$\mu_{total} = 1 - SG (0.653 + 0.01MC_d) \quad (8)$$

2.9.4. Water Absorption (WA) and Volumetric Swelling (S)

Amount of water absorbed by dry wood, when kept under moisture was calculated using equation (9) as given below:

$$WA = \frac{m_s - m_0}{m_0} \times 100 \quad (9)$$

Where:

m_s = weight of wood after soaking for 24 h (g)

Volumetric swelling of dry wood, when kept under moisture was calculated by equation (10) as given below:

$$S = \frac{V_s - V_0}{V_0} \times 100 \quad (10)$$

Where

S = volumetric Swelling (%)

and V_s = swollen volume (after soaking) (cm^3)

2.9.5. Compression Strength ($\sigma_{\max}$) and Elasticity (E)

Compression strength of wood samples conditioned to EMC of 12%, was calculated by equation (11) as given below:

$$\sigma_{\max} = \frac{F_{\max}}{A} \quad (11)$$

Where

$\sigma_{\max}$ = compression strength which is equal to maximum compressive stress (MPa).

$F_{\max}$ = maximum compressive load (MN).

and A = area (m^2) which is equal to radial dimension times tangential dimension.

Modulus of elasticity was calculated by equation (12) as given below:

$$E = \frac{\sigma}{\epsilon} \quad (12)$$

Where

E = modulus of elasticity (MPa)

σ = compressive stress (MPa).

and ϵ = compressive strain

Compressive strain was calculated by equation (13) as given below:

$$\epsilon = \frac{\Delta L}{L_1} \quad (13)$$

ΔL = the difference between final and initial length (mm) i.e. $\Delta L = L_2 - L_1$.

and L_1 = initial length (mm) before compression.

2.10. Drying Behavior

2.10.1. Moisture Ratio (MR)

Using weight data measured by TGA 701 at various time, MC of the samples during drying time was calculated. Then, moisture ratio was calculated, applying equation (14) (Chen et al., 2012) as given below:

$$MR = \frac{MC - MC_{final}}{MC_{initial} - MC_{final}} \quad (14)$$

Where:

MR = moisture ratio

MC = current moisture content (%)

MC_{final} = moisture content at the end of drying (%)

and MC_{initial} = moisture content at the beginning of drying (%).

Then, moisture ratio (MR) as a function of time elapsed was plotted for treated and untreated samples.

2.10.2. Drying Rate (R) and Overall Liquid Diffusion Coefficient (D_L)

Drying rate (R) was calculated using equation (16) (Geankoplis, 2009). Then R was plotted as a function of MR which was used to calculate overall liquid diffusion coefficient.

$$X_i = \frac{MC}{100} \quad (15)$$

$$R = \frac{dX}{dt} = \frac{1}{100} \times \frac{MC_{t1} - MC_{t2}}{t_2 - t_1} \frac{kg\ water}{kg\ dry\ solid.h} \quad (16)$$

Drying behavior comparison was performed by comparing graphs between $\frac{dX}{dt}$ and mean moisture fraction $\left(\frac{X_1 + X_2}{2}\right)$.

Unsteady state molecular transport equation for mass is written as following for three-dimensions:

$$\frac{\partial X}{\partial t} = D_L \left(\frac{\partial^2 X}{\partial x^2} + \frac{\partial^2 X}{\partial y^2} + \frac{\partial^2 X}{\partial z^2} \right) \quad (17)$$

Where D_L (m^2/s) is the overall liquid diffusion coefficient in each dimension and x , y , and z are the diffusion lengths (m).

Assuming that initial moisture distribution is uniform at $t = 0$, a simple solution to above equation (equation 17) may be written as following:

$$\frac{X}{X_1} = \frac{8}{\pi^2} \left[e^{-D_L t (\pi/2x_1)^2} + e^{-D_L t (\pi/2y_1)^2} + e^{-D_L t (\pi/2z_1)^2} \right] \quad (18)$$

Where X_1 is the initial fractional MC, x_1 , y_1 , and z_1 are half of the length, width, and depth (m) of the sample. Solving above equation (Equation 18) for time of drying will result equation 19.

$$t = \frac{4}{\pi^2 D_L} \ln \left(\frac{8X_1}{\pi^2 X} \right) [x_1^2 + y_1^2 + z_1^2] \quad (19)$$

In the equation 19, if the diffusion mechanism started at $X = X_C$, then $X_1 = X_C$. Differentiating Equation 19 with respect to time and rearranging resulted in following expression:

$$\frac{dX}{dt} = - \frac{\pi^2 D_L X}{4[x_1^2 + y_1^2 + z_1^2]} \quad (20)$$

Therefore, slope of $\frac{dX}{dt}$ versus X will be $\frac{\pi^2 D_L}{4[x_1^2 + y_1^2 + z_1^2]}$. The overall liquid diffusion coefficient is calculated from the slope. The values of X range from the FSP to zero. With each temperature increase of 1°C , FSP decreases by 0.1%. The FSP at different temperatures can be determined using the following relation:

$$\text{FSP} = [0.3 - 0.001 (T - 20)] \times 100 \quad (21)$$

Where

FSP = the fiber saturation point (%)

and T = the temperature (°C)

Hence, when the temperature is at 20°C, the value of FSP is equal to 30%. In similar fashion, at 105°C, the value of FSP is assumed to be 21.5% (Stamm and Loughborough, 1935; Siau, 1995; and He et al., 2012).

2.11. Statistical Analysis

Two-way Analysis of Variance (ANOVA) based on two-by-two factorial design was applied to make statistical comparison between different treatments and the effect of temperature (100°C and 140°C), media (HCW and steam), and interaction of them on physical characteristics of wood samples. In case of significant interaction effect, ANOVA was followed by multiple comparison on least square means, with Tukey adjustment. In addition, one-way ANOVA was done to compare five groups of the samples including control group and four treated groups, followed by the least significant difference (LSD) multiple comparison. ANOVA was done at confidence level of 95% which is 5% of significance level. Data were analyzed using JMP and SAS software (JMP®, Version Pro 12.2, SAS Institute Inc., Cary, NC).

Additional possible source of variability among the wood samples was the wood maturity. It was not accounted for in the design of this experiment and consequently, some replicates contained juvenile wood samples, while others did not. However, the homogeneity of replicates was evaluated to see if the juvenile samples increased the variability, caused lack of normal distribution, or if they were the outliers that should be excluded. Shapiro-Wilk test was utilized to check the goodness-of-fit of normal distribution for each replicate (group of 6 wood blocks). Shapiro-Wilk test is a goodness-of-fit test that can be utilized to check various continuous distributions to detect the departures from the expected fit. Most of the statistical modeling utilize

parametric methods and require normal distributions of residuals. Therefore, it is necessary in analytical process to have available tools for testing this distributional assumption. Tests of normality offered in the statistical journals that focus on compound null hypothesis are referred to as the goodness-of-fit statistic tests. According to Coin et al. (2008) goodness-of-fit statistic tests available can be clustered into four main categories: 1) tests based on the distance between the theoretical distribution function and the observed distribution function; 2) methods derived by linking Skewness and Kurtosis; 3) group of tests utilizing Pearson's Chi-square; and 4) the tests based on regression methods.

Evaluations and recommendations of the various methods for testing the normality were done by Shapiro et al. (1988), Pearson et al. (1977), in addition to D'Agostino and Stephens (1986). They used simulations to derive an empirical power of many tests against many different alternative distributions. The general conclusions of these works recommended the Shapiro-Wilk W test by and large superior test of non-normality (Coin et al., 2008).

Chapter 3. Results and Discussion

3.1. Determination of the Maturity of Wood Samples

It is well known that juvenile wood has different physical and mechanical properties than mature wood mostly because of different specific gravity, fiber length, and thickness of cell wall (Bowyer et al., 2007). This variation can affect the result of treatments on wood. In current research, there was a concern that some samples (11 specimens), which come from the zone closer to pith might contain juvenile wood. However, the acceptability of data was proven through two different ways. First, specific gravity did not show any noticeable difference among wood samples. Secondly, Shapiro Wilk test did not show any lack of normality between the replications having “so-called juvenile” samples and the replications free of “so-called juvenile” samples.

Table 1. Frequency of juvenile wood in different replications.

Treatment	Replication	Frequency of “so-called juvenile” wood
Control	1	0 out of 2
	2	0 out of 2
	3	0 out of 2
HCW at 100°C	1	0 out of 6
	2	0 out of 6
	3	0 out of 6
HCW at 140°C	1	2 out of 6
	2	1 out of 6
	3	0 out of 6
Steam at 100°C	1	0 out of 6
	2	0 out of 6
	3	0 out of 6
Steam at 140°C	1	6 out of 6
	2	2 out of 6
	3	0 out of 6
Total	-	11 out of 78

As can be seen in Table 1, totally 14% (11 out of 78) of the samples came from “so-called juvenile” wood and the rest of the samples (67 out of 78) came from mature part of the log. All the “so-

called juvenile” samples were found in two groups of treatment including HCW at 140°C and steam at 140°C. In details, first and second replications of HCW at 140°C had two and one “so-called juvenile” samples, respectively. Moreover, first and second replications of steam at 140°C, in turn, had six and two “so-called juvenile” samples.

3.1.1. Consistency of Specific Gravity

On an average, green specific gravity of the samples treated in HCW at 140°C showed consistent values, that is, 0.43, 0.42, and 0.42 for the first, second, and third replications. Also, first, second, and third replications showed oven-dry specific gravity of 0.49, 0.48, 0.50, respectively, which again did not show any noticeable difference. Likewise, neither green nor oven-dry specific gravity showed considerable changes among replications of the samples treated in steam at 140°C. In details, first replication, second replication, and third replication had oven-dry specific gravity 0.49, 0.50, and 0.59, respectively. In literature, green specific gravity of yellow-poplar reported 0.40, which is even lower in “so-called juvenile” wood, depending on the distance to pith. Furthermore, the average green specific gravity of the samples come from the first (11 specimens) and second groups (67 specimens) were same (0.43), while oven-dry specific gravity of the samples come from the first and second groups were 0.49 and 0.50, respectively.

3.1.2. Normality of the Results for Different Properties among Experimental Replications

Shapiro Wilk test revealed that for data on elasticity, shrinkage and swelling, and dry-basis moisture content, all replications in every treatment followed normal distribution, i.e. (p-value > 0.05), which means the samples cut from the proximity to the pith wood did not produce outlier data.

Abnormality of data was observed for some properties in some replications, which had no “so-called juvenile” wood. Concerning specific gravity, SG_0 of first replication of HCW at 100°C (p-

value = 0.006), first replication of steam at 100°C (p-value = 0.029), and third replication of steam at 100°C (p-value = 0.031) were not normally distributed. Moreover, SG of third replication of steam at 100°C (p-value = 0.003) was not normally distributed. All aforementioned replications were free of “so-called juvenile” wood. Likewise, regarding diffusion coefficient, second (p-value = 0.043) and third (p-value = 0.023) replications of HCW at 100°C were both not normally distributed. These two distribution did not include any “so-called juvenile” specimens.

In terms of water absorption, first replication of steam at 140°C (p-value = 0.002), third replication of HCW at 100°C (p-value = 0.001), and third replication of HCW at 140°C (p-value = 0.037) did not show normal distribution among which, only first replication of HCW at 140°C had “so-called juvenile” samples. Similarly, on the subject of porosity, first replication of steam at 140°C (p-value = 0.005), second replication of steam at 140°C (p-value < 0.001), and third replication of HCW at 140°C (p-value = 0.030) did not show normal distribution among which, the first and second replications of steam at 140°C had juvenile samples.

Occurrence of not normally distributed samples in replications having “so-called juvenile” wood was three out of 40 (7.5%), which was less than that of all replications not having “so-called juvenile” samples, that is, 10 out of 110 (9.1%). Besides, occurrence of not normally distributed samples in replications having “so-called juvenile” wood is less than that of all replications not having juvenile samples in same treatment groups that contained the “so-called juvenile” samples. In addition to above comparisons, even from a conservative point of view, 7.5% itself is really low for Shapiro-Wilk test.

3.1.2. Acceptability of the Data

Therefore, it is verified that the “so-called juvenile” samples (11 specimens come from the first group) were, in fact, mature wood samples. There are two reasons to support this conclusion. First,

the replications which have samples from closeness to pith did not show reduced specific gravity compared to the ones come from proximity to sapwood. Secondly, all the replications showed greater specific gravity than the value reported in literature for juvenile yellow-poplar (Forest Product Laboratory, 2010). Additionally, Shapiro Wilk test verified that the “so-called juvenile” specimens were more likely mature than that of juvenile wood.

3.2. Physical Characteristics

3.2.1. Moisture Content and Volumetric Shrinkage

On an average, the green yellow-poplar samples had moisture content of 43.6 ± 0.8 (Table 3), which was lower than that reported for green yellow-poplar heartwood (83%) (Simpson and TenWolde, 1999). The lower green moisture content in the test samples may be attributed to several factors, such as, geographic location, harvest season (Manwiller, 1975), tree diameter (Zobel and Van Buijtenen, 2012) and time elapse between tree harvest and sample processing due to natural air drying.

Table 2. MC (dry basis) and volumetric shrinkage (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Treatment (media and temperature)	Dry-basis MC before (%)	Dry-basis MC after (%)	Volumetric Shrinkage (%)
Untreated (control)	43.6 ± 0.8	43.6 ± 0.8^d	12.4 ± 0.6^b
HCW 100°C	46.6 ± 3.0	85.5 ± 11.8^b	11.5 ± 0.6^b
HCW 140°C	46.0 ± 1.4	101.1 ± 6.7^a	13.7 ± 0.8^a
Steam 100°C	50.9 ± 1.1	71.9 ± 3.7^c	11.6 ± 0.6^b
Steam 140°C	50.1 ± 4.6	69.6 ± 9.9^c	12.4 ± 0.4^b

Note: superscripts letter show statistical significance.

In literature, samples of poplar and Manchurian walnut with thickness of 2 cm, which were used for steam treatment, had initial MC of 122.8% and 91.9%, respectively (Peng et al., 2012). In another research, Cai (2006) used samples of subalpine fir at initial MC of 67.6% for steam explosion treatment. Overall, the hydrothermal treatment increased MC of samples. For example,

processed samples in HCW at 140°C increased MC from 46.0% to 101.1%. Likewise, processing samples in steam medium at same temperature increased MC from 50.1% to 69.65% (Figure 19). The increase in MC as a result of hydrothermal treatment may be explained by changing in hydrogen bonding intensity of hydroxyl group and changes in crystallinity (Dadashian et al., 2005 and Singh and Sivanandan, 2014). Heating fibers up to 70-80°C decreases intramolecular hydrogen bonding (Dadashian et al., 2005), which results in higher crystallinity (Singh and Sivanandan, 2014). However, heating fibers beyond 130°C results in significant increase in hydroxyl group intensity resulting in reduced crystallinity and therefore more water absorption capacity. Singh and Sivanandan (2014) reported that crystallinity of yellow-poplar wood is about 0.73, which increases to 1.75 when treated hydrothermally at low temperatures and after that drops to 0.74 when treatment temperature reaches 250°C.

Figure 19. MC (dry basis) (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Our observation of increased MC is contradictory to the results reported by Peng et al. (2012) and Cai (2006). In the current research, the media of hydrothermal treatment had significant effect on MC (p -value = 0.001). The HCW medium reached MC as high as 101.1, whereas steam medium

increased MC up to 71.9%. Additionally, the temperature level did not have significant effect on MC (P-value= 0.137). Effect of medium may be justified by the fact that liquid medium facilitates better access of water molecules to the smaller pores than steam medium (Siau, 1995 and Siau, 1984). Both Peng et al. (2012) and Cai (2006) have reported decrease in MC as results of steam treatment and steam explosion, which are not in favor of the result of current research. Peng et al. (2012) reported that steam treatment at 100°C and 140°C decreased MC of poplar samples. In Peng's research, poplar had initial MC of 122.8% and 91.9% to start with, which became 89.8% after steam treatment at 100°C and 71.9% after steam treatment at 140°C.

Contrary to the results of the literature, in our research, steam treatment increased MC of the samples which is owing to different steaming process. In our research, steam was not injected nor released instantaneously. As a matter of fact, the steam was generated in the sealed reactor by heating up the water inside the vessel. Post one hour of holding time, temperature (and consequently the capacity of the medium to hold moisture) decreased during cooling down phase, which took about 20 min and 35 min for treatments at 100°C and 140°C, respectively. Wood samples could absorb moisture during the cooling down phase.

Wood shrinks as its MC drops below FSP. Linear shrinkage varies in three different directions (longitudinal, radial, and tangential) due to anatomical characteristics. Therefore, volumetric shrinkage has been calculated to represent overall shrinkage for control and hydrothermally treated samples. Volumetric shrinkage (Table 2) (Figure 20) represents average volumetric shrinkage in samples when control and treated samples were oven-dried. The control sample of yellow-poplar showed 12.4% of volumetric shrinkage when it was dried from 43.56% to zero percentage of MC. The volumetric shrinkage demonstrated by the control sample was equivalent to that reported by Simpson and TenWolde (1999), that was 12.7%.

Additionally, all treatments but HCW at 140°C did not affect volumetric shrinkage. The samples treated in HCW medium at 140°C showed increased volumetric shrinkage of 13.7%. Statistical analysis showed that medium had significant effect on volumetric shrinkage (p-value = 0.004); however, effect of temperature on shrinkage was minimal (p-value = 0.147).

In literature, only the effect of steam medium and temperature on shrinkage have been reported (Alexiou et al., 1990 and Cai, 2006). Similar to the results of this research, Alexiou et al. (1990) observed no significant change in volumetric shrinkage of eucalyptus (*pilularis Sm.*) when it was steamed at 100°C for 3 h prior to drying. On an average, volumetric shrinkages of the steamed and control eucalyptus samples were 19% and 20%, respectively.

Cai (2006) focused on linear shrinkage (width and thickness) of subalpine fir for steam explosion treated samples at 120°C, 130°C, and 160°C, which was followed with conservative and accelerated drying schedules. Results showed that wood samples heated up to 130°C had demonstrated linear shrinkage similar to control samples (about 2.6% for width and 2.7% for thickness). However, fir samples treated at 160°C (maximum pressure of 6.2 bar) demonstrated significantly higher shrinkage in both width (3.6%) and thickness (4.0%). It appears that beyond temperature of 140°C, the effect of temperature does become significant. However, our preliminary test samples treated in HCW at 160°C became very brittle, which created inaccurate dimension measurement. For this reason, treatments in HCW above 140°C were not chosen for real test.

Figure 20. Volumetric shrinkage (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

3.2.2. Specific Gravity

Typically, green and oven-dry specific gravity for yellow-poplar are reported to be 0.40 and 0.46, respectively (Forest Product Laboratory, 2010), which are fairly lower than the values reported in this research. This may be justified by the fact that all samples used in the current research were from heartwood, which typically has lesser porosity and more density than sapwood (Hoadley, 1980 and Hoadley, 1980). In this research, samples used to perform various hydrothermal treatments had green SG of 0.44, which upon oven-drying increased to 0.50 at zero MC (Table 3) (Figure 9 and 10).

Table 3. Green specific gravity and oven-dry specific gravity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Treatment (media and temperature)	Green specific gravity	Oven-dry specific gravity
Untreated (control)	0.44 $\pm$ 0.01	0.50 $\pm$ 0.14
HCW 100°C	0.44 $\pm$ 0.01	0.49 $\pm$ 0.17
HCW 140°C	0.42 $\pm$ 0.01	0.49 $\pm$ 0.13
Steam 100°C	0.44 $\pm$ 0.02	0.50 $\pm$ 0.18
Steam 140°C	0.43 $\pm$ 0.02	0.49 $\pm$ 0.19

Figure 21. Green specific gravity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

SG values did not change significantly as results of various hydrothermal treatments. Statistically, neither of the treatment factors (temperature and medium) had significant effect on SG. It may be noted that any change in SG is expected from change in volume, which is the denominator of equation (5 and 6), given no loss of mass was taken place. While for HCW at 140°C, volumetric shrinkage was significantly higher than the other groups, it did not change oven-dry volume considerably. In the current treatment conditions, both green volume and oven-dried mass remained unchanged. The main effect of media (p-value = 0.224), main effect of temperature (p-value = 0.099), and interaction effect of media and temperature (p-value = 0.529) were statistically insignificant. In current research, no significant loss of mass was recorded under treatment temperature of 140°C. Literature suggests that wood undergoes significant loss of mass when treated at temperatures above 170°C, which significantly affects SG (Gunduz et al., 2008 and Yang et al., 2007). All wood polymers are very stable below 155°C. The glass transition temperature of lignin is 160°C (Dawn, 1987). As temperature reaches 160°C, lignin starts to melt (Yang et al., 2007). Beyond temperature of 160°C, carbonyl groups present in lignin detach from its aromatic

rings (Singh and Sivanandan, 2014). Further increase in temperature up to 220°C leads to decomposition of hemicellulose. Chemical changes in cellulose take place beyond 315°C, at which cellulose does experience irreversible structural change (Hatakeyama and Hatakeyama, 1979) that was led to appearance of a new infrared spectral transmittance peak at the wavenumber 1590 cm^{-1} that is related to the hydrogen bonding formation in amorphous cellulose. The relative intensity of absorbance at wavenumbers of 1590 cm^{-1} and 3400 cm^{-1} with respect to 2900 cm^{-1} were used by Hatakeyama and Hatakeyama (1974) to reveal changes in total hydrogen bonding and the formation of new hydrogen bonding.

Overall, Dashti et al. (2012a) reported reduction in holocellulose content of aleppe oak from 67.20% to 62.40%; lignin content from 28% to 27%, and water soluble extractives content from 4.84% to 3.85% as a result of steam treatment at 160°C. Therefore, no change in SG of yellow-poplar is in agreement with literature due to the fact that no significant loss of mass or volume change took place during our treatment conditions.

Figure 22. Oven-dry specific gravity (mean ± standard error) of untreated and hydrothermally treated yellow-poplar.

3.2.3. Porosity

The total porosity represents fraction of green volume, which is not occupied by wood cell mass. The control samples showed that about 82.4% of the green volume was occupied by either air or water and only 17.4% of the green volume was occupied by dry wood mass (Table 4). Total porosity of oven-dried wood of varying specific gravity has been documented using mercury intrusion porosimetry, which range from 73.7% for wood having specific gravity of 0.40, to 22.11% for wood having specific gravity of 1.16. Total porosity has been reported to be 68.00% for wood having specific gravity of 0.48 (Plotze and Niemz, 2011). Theoretically, total porosity (μ) may be calculated using equation (8) as given earlier (Siau,1995). Theoretical value for porosity samples tested in the current research is 71.3%, which was close to the measured values.

Table 4. Total porosity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar

Treatment (media and temperature)	Total porosity (%)
Untreated (control)	82.4 $\pm$ 1.8 ^b
HCW 100°C	83.3 $\pm$ 4.0 ^b
HCW 140°C	92.2 $\pm$ 3.4 ^a
Steam 100°C	92.3 $\pm$ 2.1 ^a
Steam 140°C	94.9 $\pm$ 2.7 ^a

Note: superscripts letter show statistical significance.

Hydrothermal treatment significantly changes total porosity of yellow-poplar samples (Figure 23). Treatments with HCW medium increased total porosity from 82.4% to 92.2% at the temperature of 140°C whereas treatment under steam increased total porosity at even low temperature of 100°C. Media (p-value = 0.022) and temperature (p-value = 0.021) significantly influenced the total porosity. However, the interaction effect of temperature and media was not significant (p-value = 0.165).

Figure 23. Total porosity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Heating dry wood samples up to 200°C for 4 hours under nitrogen has varying effects on its total porosity. While thermal modification of dry spruce wood reduced total porosity from 71.9% to 69.7%, it increased from 65.7% to 66.6% for maple wood and it did not change at all for ash wood (Zauer et al., 2013). Zauer et al. (2013) also claimed that this type of thermal modification of wood leads to decreased nano-pore shares, below a pore diameter of 400 nm, and decreased FSP because the proportion of capillary condensed water in thermally modified wood reduced significantly. Enhanced porosity due to thermal treatment could be due to fractured cell-wall, loss of extractives, and decay of cell-wall constituents. Hydrothermal treatments at high temperature is shown to have produced more voids and fractures (Biziks et al., 2013). Biziks et al. (2013) also reported that the lumen cross-section decreased by 2.3%, while the tangential length of the lumen decreased by 0.5% and the radial length of the lumen decreased by 2.7%. In contrast, the cross-sectional area of the fibers decreased from 1.0% at 140°C and 20.7% at 180°C mainly due to degradation of cell wall constituents

Steam explosion on Chinese fir creates several changes in wood constituents. Treatments equal to or below temperature of 120°C, pressure of 2.5 bar with ten cycles did not cause considerable changes in wood structure while treatment with temperature of 130°C, pressure of 2.5 bar with 20 cycles caused some fractures in bordered pit pairs between tracheids. More considerably, temperature of 160°C, pressure of 6.2 bar with 10 cycles caused more fractures in border pit pairs (Zhang and Cai, 2006). Likewise, micro-explosion created several fine fractures on the weak parts of the cells, i.e. the pit membranes, as a result of an instantaneous exhaust process

3.2.4. Water Absorption and Volumetric Swelling

To measure water absorption (WA) capability, post hydrothermal treatment, the treated-dried samples were submerged in water for 24 h. After 24 h, amount of water absorbed and volumetric swelling were measured. The hydrothermal treatments significantly changed water absorption (WA) capability and total volumetric swelling (Table 5) (Figure 24 and 25).

Table 5. Water absorption and volumetric swelling (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Treatment (media and temperature)	Water absorption (%)	Volumetric swelling (m ² /s)
Untreated (control)	32.5 $\pm$ 0.9 ^b	12.2 $\pm$ 0.5
HCW 100°C	38.2 $\pm$ 3.0 ^b	12.1 $\pm$ 0.5
HCW 140°C	48.8 $\pm$ 9.9 ^a	11.6 $\pm$ 0.9
Steam 100°C	41.1 $\pm$ 3.5 ^a	12.7 $\pm$ 0.8
Steam 140°C	45.8 $\pm$ 5.8 ^a	10.0 $\pm$ 1.0

Note: superscripts letter show statistical significance.

Figure 24. Water absorption (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

WA after 24 h soaking for untreated yellow-poplar heartwood samples was 32.5%, which was significantly below the WA values of treated samples. Upon hydrothermal treatments, the WA significantly increased for all treatments except HCW at 100°C. This results tally with porosity values indicating that hydrothermal treatments boost porosity and consequently WA. Among treatment factors, the temperature had significant influence on water absorption (p-value = 0.013); however, media had minimal effect (p-value = 0.995). Besides, interaction effect of temperature and media was not significant (p-value = 0.253).

In literature, comparison of WA of untreated and hydrothermally treated wood has been reported (Dundar et al., 2012; Tuong and Li, 2011; and Scheilding et al., 2006). Dundar et al. (2012), compared water sorption and water repellent effectiveness (WRE) of untreated and hydrothermally treated black pine at 180°C and 210°C. They reported that WA was 108.1% for the control samples, which reduced to 104.3% after testing samples at 180°C. Treatment at 210°C further reduced WA (to 74.3%). In another research, Tuong and Li (2011) heated acacia sapwood in nitrogen at temperatures of 210°C, 215°C, 220°C, and 230°C for 2, 4, and 6 h and tested heat treated samples for WA. They reported that WA of treated samples decreased significantly with

increase of treatment time and temperature. For example, treating acacia wood at 210°C for 2 h reduced WA from 135% to 125%.

In these research reports, the reduction in WA was attributed to reduction of hydroxyl group in wood (Weiland and Guyonnet, 2003 and Tjeerdsma and Militz, 2005) or owing to formation of cross-linking over heat treatment, which makes the molecules less elastic, decreasing the possibility to enlarge the cellulose microfibrils (Tjeerdsma et al., 1998). While literature showed decrease in WA, temperature used in current research were not high enough to make aforementioned changes.

Figure 25. Volumetric swelling (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Like WA, the volumetric swelling of untreated and treated samples was also measured when the dry samples were soaked in water for 24 h. Volumetric swelling after 24 h for untreated yellow-poplar heartwood samples was 12.2%. Theoretically, maximum volumetric swelling may be calculated by multiplying 30 with oven-dried specific gravity. For the current research samples, the untreated samples had oven-dry specific gravity of 0.50, which would result in 15.0%

theoretical volumetric swelling. Our measured volumetric swelling was 12.2%, lower than the theoretical value probably due to lack of significant time (24 h) for complete saturation of wood samples. Longer saturation duration would have achieved volumetric swelling close to the theoretical value.

All hydrothermal treatments did not significantly change volumetric swelling. Meanwhile, main effect of temperature (p-value = 0.053) and media (p-value = 0.499), as well as their interaction effect (p-value = 0.144) on shrinkage were all insignificant. However, steam treatment at 140°C reduced volumetric swelling from 12.2% to 10.0%. In literature, Dundar et al. (2012) compared volumetric swelling and anti-swell effectiveness (ASE) of black pine samples hydrothermally treated at 180°C and 210°C. They report that the volumetric swelling values after 24 h immersion time were 10.4 % for control samples, which reduced to 7.9% and 6.5% after hydrothermal treatment at 180°C and 210°C, respectively. In another research, Tuong and Li (2011) reported volumetric swelling of 13.2%, which reduced to 9.5%, 9%, 8%, and 6.5% following 2 h of heat treatment at 210°C, 215°C, 210°C, and 230°C. Same trend of reduction was observed for radial and tangential shrinkage as well

3.3. Mechanical Properties

Compression strength and modulus of elasticity are perhaps key mechanical properties of wood to be used in structural applications. The yellow-poplar wood samples which had been conditioned to reach 12% of EMC showed compression strength of 42.95 MPa (Table 6) and modulus of elasticity of 1.29 GPa (Figure 26). In the wood hand-book, the compression strength of yellow-poplar has been reported to be 38.20 MPa (along the grain), which slightly lower than our test samples (Figure 27) (Forest Product Laboratory, 2010).

Table 6. Modulus of elasticity and compression strength (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Treatment (media and temperature)	Modulus of Elasticity (GPa)	Compression Strength (MPa)
Untreated(control)	1.29 ± 0.10^c	42.95 ± 2.79^{abc}
HCW 100°C	1.66 ± 0.13^a	47.75 ± 2.33^a
HCW 140°C	1.36 ± 0.14^{bc}	43.73 ± 3.78^{ab}
Steam 100°C	1.17 ± 0.10^c	38.50 ± 3.78^c
Steam 140°C	1.57 ± 0.18^{ab}	42.27 ± 2.46^{bc}

Note: superscripts letter show statistical significance.

Figure 26. Modulus of elasticity (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Hydrothermal treatment significantly increased the modulus of elasticity of yellow-poplar. For example, the modulus of elasticity increased from 1.29 GPa (control) to as high as 1.66 GPa due to hydrothermal treatment performed in HCW medium at 100°C. Also, steam treatment at 140°C led to increase in modulus of elasticity. In literature, Dundar et al. (2012) reported modulus of elasticity of black pine wood (thermally treated at 180°C and 210°C). According to the report, the modulus of elasticity significantly decreased from 5.6 GPa (control) to 4.78 GPa when samples were treated at 180°C. Further increase in temperature did not change modulus of elasticity. In literature, most of the treatments are performed well beyond 140°C which is the maximum

temperature used in the current research. Therefore, literature data may not be used to cross verify the results presented in Table 6.

In the current research, the interaction effect of temperature and medium was significant (p-value = 0.001) because of two reasons. On the one hand, modulus of elasticity had significantly lower values for steam at 100°C compared to HCW at steam at the same temperature (p-value = 0.004); on the other hand, modulus of elasticity increased significantly following elevation of temperature in steam medium (p-value = 0.016).

Figure 27. Compression strength (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Influence of medium and temperature on the compression strength of yellow-poplar followed a pattern similar to the modulus of elasticity. Compression strength of yellow-poplar heartwood was 42.95 MPa, which increased with the hydrothermal treatments, in general, except for steam treatment at 100°C.

Statistically, the main effects of temperature and medium were insignificant (P-value = 0.933) and significant (P-value = 0.007), respectively. In addition, interaction effect of temperature and media was significant (P-value = 0.031). The significance of interaction effect is due to the fact that there

is a considerable difference between HCW and steam at 140°C (P-value = 0.001) while these two different media did not have noticeable difference at 140°C. In literature, Dundar et al. (2012) reported significant decrease in modulus of rupture, from 61.4 GPa (control) to 43.0 GPa, due to hydrothermal treatment at 180°C for black pine wood.

3.4. Drying Behavior and Overall Liquid Diffusion Coefficient

The drying behavior of the wood samples was analyzed into two sets of graphs. In the first set, moisture ratio (MR) was plotted as a function of drying time, which provides crucial information about how fast material dries. In the second set, drying rate was plotted as a function of moisture ratio, which provides insight into prevailing mechanism of moisture loss and overall liquid diffusion coefficients. The following sub-sections provide details of drying behavior.

4.4.1. Drying Time and Moisture Ratio

Moisture ratio (fraction of initial moisture left) at given time was plotted for the control and hydrothermally treated samples (Figure 28). A quick observation of the figure 16 shows that the drying behavior line (MR vs time) for HCW treated samples lies above the drying behavior line for control samples; however, drying behavior line for steam treated samples is close to but below the drying behavior line of control samples. It essentially means that it takes longer and slower to dry HCW treated samples than control whereas steam treated samples dry faster. Both steam treated samples follow similar drying behavior.

Figure 28. Moisture ratio as a function of time elapsed during drying at 105°C for untreated and hydrothermally treated samples of yellow-poplar.

Additionally, high temperature (140°C) HCW treated samples held moisture more tightly than low temperature (100°C) HCW treated samples. Holding high moisture ratio at a given drying time indicates two factors: 1. Moisture was held with more binding forces and 2. Pores were blocked slowing down mass transfer rate. Taghiyari et al. (2011) reported that treating beech at 180°C in hot water leads to extra extractives settlement on perforation plates and cell walls, which slows mass transfer rates during drying. In contrast, steam treated samples possess pores and cavities with less blockage, therefore dry faster than the control samples. According to Peng et al. (2012), the bound water diffusion was slower in the samples steam treated at 100°C or 140°C than the control samples of poplar wood. They report that the total drying time of poplar boards of 6 cm was 102 and 74 h for untreated and treated samples, respectively. In the current research, total time for the samples to reach zero MC was dependent on type of treatment.

As can be observed in Table 7, untreated samples reached zero MC after 226 min, which was faster than treated samples. Steam treated samples at either temperature did not show noticeable longer time to be oven-dried. However, samples treated in HCW at 140°C showed the longest drying time (260 min). Increased drying time for the treated samples in HCW at either temperature can be explained by elevated MC of the samples which experienced hydrothermal treatment in liquid medium. Regarding the uniformity of drying time, control samples showed the most uniform drying time (standard deviation = 0.02). However, statistically hydrothermally treated samples did not show significant change from the control samples. In addition, all the effects of temperature (p-value = 0.130) and media (p-value = 0.180) and the interaction of them (p-value = 0.616) were insignificant.

Table 7. Drying time (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar to reach zero MC.

Treatment (media and temperature)	Drying time (min)
Untreated (control)	225.95 $\pm$ 0.02
HCW 100°C	240.40 $\pm$ 4.48
HCW 140°C	260.14 $\pm$ 12.76
Steam 100°C	231.94 $\pm$ 9.07
Steam 140°C	242.35 $\pm$ 13.19

4.4.2. Drying Curve

Drying behavior (moisture desorption) from wood in zero humidity and constant temperature is associated with wood properties, such as, various pore sizes, affinity of wood for water, total porosity, density, and specific gravity. Moisture desorption from wood is fundamentally controlled by two simultaneous mechanisms, which are capillary flow and diffusion flow (Siau, 1995 and Simpson, 1991). In Figure (29), following four phases are observed: First- increase in drying rate

due to sample heating; second- linear capillary controlled (convective) falling phase; third- non-linear transition falling phase, and fourth- linear diffusion controlled falling period.

Figure 29. Drying rate as a function of moisture ratio for untreated and treated samples of yellow-poplar.

Over the second phase of drying, free water flows through the cell lumens and pits due to capillary action. In the third phase, moisture loss takes place from lumens (free water) as well as from cell wall (bound water). In the fourth phase, when cell lumens and pits become empty, water vaporizes from cell wall and water vapor flows through the cell lumens and pits by diffusion. Bound water also diffuses through the cell walls. Diffusion coefficient of water vapor is three to four orders of magnitude smaller in lumens than water vapor diffusion coefficient in free water (Siau, 1995). It is also worth noting that almost in most of studies on wood and water relation, type of diffusion has been neglected and diffusion is presented based on Fickian type of diffusion while Kundsén diffusion would dominate for small pore openings. In actuality, large lumens may comply with

Fickian diffusion; whereas, small pits and lumens may conform to Kundesen diffusion (Geankoplis, 2003).

The drying rate curve presented in the Figure 18 has several obvious observations. First, drying rate curves of all the hydrothermally treated samples were above the drying curves of controlled samples because the treated samples had high initial moisture content (Table 7). Therefore, higher amount of water was evaporated at given moisture ratio from treated samples than that from control samples. In the drying curves, slopes of the drying curves in various phases are important because it is used to calculate overall liquid diffusion coefficients. In the current research, overall liquid diffusion coefficients was calculated for the convective controlled drying phase. Notwithstanding, HCW treatment especially at elevated temperature exhibited greater drying rate than control. Difference in drying rate is predominantly attributed to total porosity.

Overall liquid diffusion coefficient of yellow-poplar heartwood was $3.18 \times 10^{-8} \text{ m}^2/\text{s}$ (Table 8) (Figure 30). Diffusion coefficient of wood has reported by numerous researcher. Sayar and Tarmian (2013) measured diffusion coefficient of poplar (*Populus nigra* L.) on account of Fick's law of diffusion in steady-state conditions using cup method. Reported values ranged from 1.34×10^{-9} to $1.90 \times 10^{-8} \text{ m}^2/\text{s}$. Using same method, Dashti et al. (2012a) reported of diffusion coefficients of alpee oak (*Quercus infectoria*) as 2.35×10^{-7} and $3.60 \times 10^{-7} \text{ m}^2/\text{s}$ for heartwood and sapwood, respectively. Shahverdi et al. (2013) reported diffusion coefficient of beech heartwood $8.16 \times 10^{-11} \text{ m}^2/\text{s}$, using cup method. He et al. (2014) calculated effective water diffusivity of Chinese fir (*Cunninghamia lanceolata*) according to the linear relationship extracted from the $\ln \text{MR}-t$ plot and based on Fick's second law and reported value of $1.34 \times 10^{-8} \text{ m}^2/\text{s}$. Using same way, He et al. (2013) measured effective water diffusion coefficients of Chinese catalpa. Values in range of 2.89 to $2.91 \times 10^{-8} \text{ m}^2/\text{s}$ for MC above FSP and values in range of 1.06 to $1.12 \times 10^{-8} \text{ m}^2/\text{s}$ for MC

below FSP were reported. Water vapor diffusion coefficients vary upon cell wall thickness and the amount of substance it contains, that is, density (Perre, 2007 and Tarmian et al., 2012). In addition, presence of hemicellulose would improve diffusivity through wood (Siau, 1984 and Tarmian et al., 2012).

Table 8. Overall liquid diffusion coefficient (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Treatment (media and temperature)	Overall liquid diffusion coefficient (m^2/s)
Untreated (control)	$3.15 \times 10^{-8} \pm 1.19 \times 10^{-9}$ ^a
HCW 100°C	$2.15 \times 10^{-8} \pm 3.65 \times 10^{-9}$ ^c
HCW 140°C	$1.89 \times 10^{-8} \pm 2.42 \times 10^{-9}$ ^c
Steam 100°C	$2.62 \times 10^{-8} \pm 1.63 \times 10^{-9}$ ^b
Steam 140°C	$3.04 \times 10^{-8} \pm 3.93 \times 10^{-9}$ ^a

Figure 30. Overall liquid diffusion coefficient (mean $\pm$ standard error) of untreated and hydrothermally treated yellow-poplar.

Hydrothermal treatments tend to reduce overall liquid diffusion from wood. Hydrothermal treatments at low temperature (100°C) reduced overall liquid diffusion coefficient from 3.18×10^{-8} to $2.15 \times 10^{-8} \text{ m}^2/\text{s}$ for HCW and $2.62 \times 10^{-8} \text{ m}^2/\text{s}$ for steam conditions, which indicated that significantly more pores were blocked with HCW treatment than steam treatment due to

mobilization of extractives. Treatment at relatively high temperature (140°C) improved overall liquid diffusion coefficient due to volatilization of extractives.

Dashti et al. (2012 b) Investigated two major transfer features i.e. air permeability and water diffusivity of untreated and steam treated fir (*Abies Alba* L.), a gymnosperm species with torus margo pit membrane. Treatments were done at different temperatures of 120°C, 140°C, and 160°C for 1 h of holding time. In spite of some contradictory observations, on the whole, both permeability and diffusivity improved following increasing temperature from 120°C to 160°C. It was claimed that this improvement is related to cell wall holocellulose hydrolysis and damage in bordered pit due to steaming. Anatomical observations following steam explosion disclosed that temperature of 120°C and pressure of 2 bar with 10 explosion cycles did not show change in tracheid walls. However, as temperature increased up to 160°C, pressure increased up to 6.2 bar, and explosion cycles increased up to 20 times, the bordered pits between tracheids were defaced and the aspirated pits were broken to different degrees based on the intensity of temperature, pressure, and explosion cycles. This was eventually leading to improvement of dryability (Cai, 2006 and Zhang and Cai, 2006).

Chapter 4. Conclusion and Summary

In this research, influence of hydrothermal treatment in steam and hot compressed water at 100°C and 140°C was evaluated on selected physical properties and drying behavior of yellow-poplar. Results showed that the moisture content of the samples greatly increased following hydrothermal treatment, which was influenced by the type of medium. Upon completely drying all the treated samples, significantly higher water absorption was observed for treated samples than the control ones. Hydrothermal treatment did not change dimensional stability (shrinkage and swelling) of treated samples, excluding steam at 140°C and HCW at 140°C, which in turn, resulted in considerable swelling reduction and noticeable shrinkage elevation. Steam treatment at 140°C is recommended because of its significant influence on swelling improvement. However, neither steam treatment nor HCW treatment is proposed to improve water repellency. Specific gravity was not influenced by the hydrothermal treatment due to zero loss of mass and insignificant amount of shrinkage for most of groups following hydrothermal treatment. Concerning mechanical properties, modulus of elasticity showed improvement following either HCW at 100°C or steam treatment at 140°C; however, no treatment resulted in change of compression strength.

Regarding drying behavior, the hot compressed water treatments resulted in slow drying due to blocked pores and elevated initial moisture content resulted from hydrothermal treatment in liquid medium. Steam treatment at relatively high temperature (140°C) improved overall liquid diffusion coefficient due to volatilization of extractives.

It is worth mentioning that this conclusion is only attributed to yellow-poplar heartwood procured from West Virginia forest. Further researches need to be carried out to reveal the effect of hydrothermal treatment on different wood species (softwoods, ring-porous and semi ring porous

hardwoods and also other diffusion porous species especially those having different specific gravity) wood component (sapwood), and type of wood (normal and reaction wood).

From practical standpoint, hydrothermal treatment (in either medium) did not hurt the final product as no reduction was observed in dimensional stability and compression strength. In addition, increased porosity and water uptake can be helpful in case wood needs to be saturated by liquid preservatives. On the whole, prior to any recommendation for industrial wood drying, further research work is needed to reveal any possible effect of hydrothermal treatments (in either medium) on warpage, checks, and splits in lumber.

Nomenclature

A = area (m^2)

D_L = overall liquid diffusion coefficient (m^2/s)

E = modulus of elasticity (MPa)

FSP = Fiber saturation point (%)

$F_{\max}$ = maximum compressive load (MN)

L_1 = initial length (mm) before compression

m = moist weight (g)

m_0 = oven-dry weight (g)

m_1 = weight of moist wood before treatment (g)

m_2 = weight of moist wood after treatment (g)

m_s = weight of wood after soaking for 24 h (g)

MC = current moisture content (%)

MC_d = dry-basis MC (%)

MC_{initial} = moisture content at the beginning of drying (%)

MC_{final} = moisture content at the end of drying (%)

MC_w = wet-basis MC (%)

MC_{w1} = Wet-basis MC before treatment (g)

MC_{w2} = Wet-basis MC after treatment (g)

MR = moisture ratio

s = volumetric shrinkage (%)

S = volumetric Swelling (%)

SG = green specific gravity at any moisture content beyond fiber saturation point

SG_0 = oven-dry specific gravity at zero moisture content

R = Drying rate ($\text{kg}_{\text{water}}/\text{kg}_{\text{dry mass}} \cdot \text{h}$)

t = time

V = wet volume of moist wood (cm^3)

V_0 = oven-dry volume of wood (after drying) (cm^3).

V_{p0} = oven-dry true volume of wood cell mass (cm^3)

V_s = swollen volume (after soaking) (cm^3)

X = fractional moisture content

x_1 = half of the length of the wood sample (m)

X_1 = initial fractional moisture content

Y = yield (%)

y_1 = half of the width of the wood sample (m)

z_1 = half of the depth of the wood sample (m)

ΔL = the difference between final and initial length (mm)

ϵ = compressive strain

μ_{total} = total porosity (%)

ρ_{water} = density of water (g/cm^3)

σ = compressive stress (MPa)

σ_{max} = compression strength (MPa)

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