1-1-2010

Utilization of extracted hardwood flakes for manufacturing oriented strand lumber

Thomas Eric McConnell

UTILIZATION OF EXTRACTED HARDWOOD FLAKES FOR MANUFACTURING ORIENTED STRAND LUMBER

By

Thomas Eric McConnell

A Dissertation
Submitted to the Faculty of
Mississippi State University
in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy
in Forest Resources
in the Department of Forest Products

Mississippi State, Mississippi

December, 2010

UTILIZATION OF EXTRACTED HARDWOOD FLAKES FOR

MANUFACTURING ORIENTED STRAND LUMBER

By

Thomas Eric McConnell

Approved:

Sheldon Q. Shi Assistant Professor of Forest Products (Co-Director of Dissertation)	Rubin Shmulsky Professor and Head of Forest Products (Co-Director of Dissertation and Graduate Coordinator)
Janice Dubien Associate Professor of Statistics (Committee Member)	Laura A. Grace Professor of Forestry (Committee Member)
Tor P. Schultz Professor of Forest Products (Committee Member)	George M. Hopper Dean of the College of Forest Resources

Name: Thomas Eric McConnell

Date of Degree: December 10, 2010

Institution: Mississippi State University

Major Field: Forest Resources

Co-Major Professors: Dr. Sheldon Q. Shi and Dr. Rubin Shmulsky

Title of Study: UTILIZATION OF EXTRACTED HARDWOOD FLAKES FOR MANUFACTURING ORIENTED STRAND LUMBER

Pages in Study: 89

Candidate for Degree of Doctor of Philosophy

Lignocellulosic ethanol production currently uses expensive and harsh methods to extract wood sugars from small-diameter hardwood trees that otherwise would have little or no marketability. A byproduct that adds no value to the conversion process results, thus alternative methods are needed to make this fuel source cost-effective. This dissertation proposes only partially hydrolyzing southern hardwoods, extracting some polysaccharides for ethanol fermentation while leaving behind a modified wood material which could be used as furnish for manufacturing strand-based wood composites. Three treating solutions, 1% sulfuric acid, water, and 1% sodium hydroxide, along with untreated controls, were utilized in a partial hydrolysis at 150°C for 30 minutes. The treatments' effects were measured by testing the mechanical, physical, surface, and durability properties of red oak, sweetgum, and yellow-poplar miniature beams (3 mm x 15 mm x 150 mm, t x r x l). These properties were then correlated to the polysaccharide content of the modified woods following treatment.

All treatments provided a significant mass loss, with sweetgum's mass loss being significantly greater than the other species. The initial effect of the partial hydrolysis on modulus of elasticity (MOE) showed water reduced MOE the least for each species. Sweetgum produced a higher reduction in MOE in all three solutions. Specific modulus was calculated to eliminate the density effect between the treatment combinations for measuring bending properties at oven-dry conditions. Sweetgum produced a lower SM in all treatments, and only the water treatment consistently reduced SM across all species.

Wettablility was measured by dynamic contact angle analysis via the Wilhelmy plate technique in four probe liquids. Surface energies were then calculated by the geometric mean procedure. Acid and water treatments improved the wettability for all species. Alkaline treatment effects were species-specific. All treatments improved the surface energy of red oak.

The AWPA E1-09 no-choice termite test determined mass loss due to *Reticulitermes flavipes* Kollar. Yellow-poplar averaged a significantly higher mass loss while wood treated in water or NaOH showed a higher degree of termite degradation compared to the controls. Polysaccharide content significantly correlated with mass loss due to treatment and specific modulus.

Keywords: mass loss, mechanical properties, partial hydrolysis, red oak, surface energy, sweetgum, termite resistance, yellow-poplar

ACKNOWLEDGMENTS

I would like to acknowledge those who helped make this dissertation possible. I want to thank the Forest Products Department and Mississippi State University for providing me the opportunity to achieve this degree. The research reported herein was financially supported by the USDA and the Southern Wood to Energy Research Group (SoWER). Rives and Reynolds of Louisville, MS kindly donated the wood for this project. Many thanks also to my committee, Drs. Sheldon Q. Shi, Rubin Shmulsky, Jan DuBien, Laurie Grace, and Tor Schultz for their guidance throughout my program of study and assisting in the preparing of this dissertation. I want to recognize the following people for their help throughout this project: Benny Green, Nate Irby, Dongping Jiang, Todd Johnson, Nathan Little, George Miller, Jenny Shi, Jinshu Shi, Linda Sites, and Dr. Bill Stuart. I greatly appreciate the constructive comments of the editors and reviewers from the journals to which these chapters have been submitted.

I am particularly grateful to my wife, Lynn, for her love and encouragement as well as my family and friends for their dedicated support.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER I

INTRODUCTION

As our population has grown, so has our need for wood and wood products (Bowyer 1995). The wood composite market in particular has increased dramatically, and a continued rise is expected over the next 50 years (Adams 2002). Wood composites are generally more flexible in raw material furnish due to the controlled processing conditions (Hammett and Youngs 2002). The structural composite lumber (SCL) products in Figure 1.1, laminated veneer lumber (LVL), parallel strand lumber (PSL), steam pressed scrim lumber (SPSL), are very efficient in their use of wood fiber, in some cases up to two times that of solid-sawn lumber (Nelson 1997). The SCL products are gaining market share as they are able to be processed from small trees and branches that are inadequate for solid-sawn lumber production. The raw material is broken down into smaller wood elements and reconstituted through material alignment, adhesion, and high pressure to produce products up to two times as dense as the original furnish (APA 2007). The end products are flexible in dimension and design as they can be processed to meet end-use specifications along with customer-specified lengths. They generally exhibit less variation and can be engineered to produce design values equivalent to or exceeding solid-sawn lumber (McNatt and Moody 1990; Knudsen 1992). For example, 1.3E oriented strand lumber (OSL, Ainsworth Lumber Co., Ltd.) has allowable bending and

tension stresses (F_b and F_t) that are nearly double that of #1 Douglas Fir-Larch solid-sawn lumber (ICCES 2007).

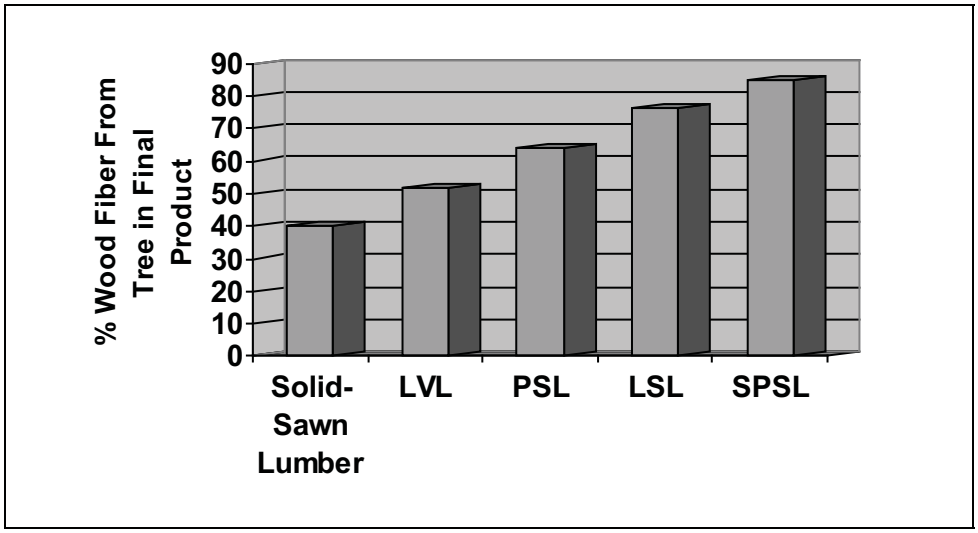

Figure 1.1

Wood use for some SCL products compared to lumber (Nelson 1997).

Problem Statement

The increasing demand for composite-based wood products, in particular SCL, has placed pressure on the current feedstock supply. The species of choice for southern composites include the various Southern Pines, *Pinus spp*. These species are readily available, their utilization has been refined through years of research, and their final products meet consumer design requirements. Southern hardwood species, such as yellow-poplar, (*Liriodendron* tulipifera L.), sweetgum, (*Liquidambar* styraciflua L.), and the red oaks, (*Quercus* spp.), are often overlooked in forest management plans in favor of high volume and fast growing pine plantations. These hardwoods are plentiful, inexpensive, and commonly associate on the same site with pines across the South.

Efforts need to be made to utilize these woods in large-scale SCL production as species diversification is vital for the SCL market to sustain its predicted growth. Tapping the abundant and under-utilized southern hardwood supply, though, is not a simple wood utilization issue.

Manufacturing constraints in SCL production due to density and adhesion, among other properties, currently limit the extensive use of southern hardwoods (Hse 1975). Lower density species are compressed more than higher density species due to thinner cell walls while many extractives found in southern hardwoods can interfere with blending and pressing (Halligan 1970; Thomas 1977). Oak is an exemplar species that prematurely gels phenol – formaldehyde (PF) resin due to the release of acidic extractives (Beech 1975). The wood – adhesive bond is thus compromised during pressing, which leads to extreme thickness changes due to lack of adhesive penetration (USDA Forest Products Lab 1999). Due to low compressive forces, the wood-adhesive bond breaks more easily as the concentration of these adhesion-interfering extractives tends to increase in hardwoods with higher density (Carll 1996). These issues, among others, need to be resolved to meet design value specifications.

Past studies have processed hardwoods into flakes for composite manufacturing. Hse (1975) examined the potential of nine hardwood species that commonly grow on southern pine sites. Density was a foremost issue as suitable flakeboards were only constructed using species with specific gravities below 0.60, principally sweetbay, red maple and sweetgum. Strength requirements could not be attained to meet dimensional stability specifications for black tupelo, white ash, red oak, hickory, post oak or white

oak. Further, only sweetgum of the suitable species has substantial forest volume in the South (Sheffield and Bechtold 1990).

Hoover et al. (1992) applied regression models to predict strength properties of OSB panels utilizing various species. Single-species and mixed-species panels were constructed out of the following woods: oak, maple, birch, ash, and aspen. Species was the most significant variable in predicting mechanical strength. Single-species panels of aspen and birch tested favorably in static bending while ash and maple had high interlaminar strength and internal bonding. An equal mixture of aspen and birch gave the highest MOE while a three species mixture of aspen, ash, and maple had the greatest internal bonding and interlaminar shear strength. Variations in the prediction of modulus were less than 5% in the aligned direction and 17% in the cross-aligned direction; internal bond and edgewise shear also varied 17%.

Modifying wood has long been looked at as a means of diversifying the raw material base as treating with heat, chemicals, or a combination of these, can overcome liabilities in processing and/or service (Paredes et al. 2009; Youngquist et al. 1986). Blankenhorn et al. (1989) examined chemically treating red oak and hard maple to enhance their properties for flakeboard manufacturing. Flakes were treated with water, sodium hydroxide or acetic acid prior to resin blending. Controls of each species along with aspen were used to evaluate changes in characteristics. Mass loss in flakes was determined to be a controllable factor in chemical modification. Press closing time was reduced for hard maple across all treatments but only after a significant mass loss in red oak. Both species' mechanical properties were reduced across all treatments.

The issue of energy and fuels has been a matter of debate since the Organization of Petroleum Exporting Countries (OPEC) oil embargo of 1973. Within the last decade the energy crisis has returned. Our dependence on foreign energy sources has been steadily increasing as foreign imports from distant and unstable regions now account for sixty percent of our national consumption (Birol 2006). Since the 9/11 terror attacks, war, renationalization in oil-rich nations, along with nationally-owned companies (NOCs) that in the past have not responded predictably to market changes has driven oil prices up as uncertainty in the market has increased (Council on Foreign Relations 2006). Domestically, hurricanes in the Gulf of Mexico in 2005 compounded the situation as oil and fuel prices peaked in 2008. As a result, corn-based ethanol production was expected to equal the amount of corn exported for the first time (Collins 2006).

Converting land to corn production to support the growing ethanol industry has had negative effects on other agricultural markets. Economic losses due to increased feed costs alone were projected to be over $500 million for the livestock industry. In the southeast U.S. alone over 700,000 acres of cotton and soybean fields were expected to be converted to corn production (Downing et al 1995). Therefore, alternative sources for biofuel production are needed.

Lignocellulosic sources for ethanol production have been proven to be readily available. The Biofuels Feedstock Development Program under the Department of Energy (DOE) found yellow-poplar and red oak to be potential feedstocks for lignocellulosic biofuel production among the 125 tree species reviewed (Tolbert and Schiller 1996). Wood sugars are fractionated through either hydro- or hygro-thermal processes for conversion to ethanol (Garrote and Parajo 1999; Schultz et al. 1983). Acids

or caustics can be added to accelerate the process (Sun and Cheng 2002). These expensive and harsh processes often completely extract the wood sugars for distillation, leaving a byproduct of little or no value for use in other manufactured goods (Hamelinck et al. 2005).

Southern forests account for over 28% of the nation's timbered land. This region provides 58% of the total U.S. harvest of timber and 60% of the total U.S. forest industry's capital expenditures (Harper 2004). A variety of hardwood forest types, primarily hardwood and hardwood – pine, cover 104 million acres, 52% of southern forest land (Sheffield and Bechtold 1990; Sheffield and Dickson 1998). Moreover, past forest management and harvesting practices have distorted age-class distributions as over 10 million acres across the South are classified as nonmanageable due to low stocking and poorly formed trees (Bechtold 1989). Better utilization of our timber resources, particularly the small-diameter hardwoods that currently have little or no marketability, would benefit not only production forestry (landowner, logger, and mill) but also the rural economies in which each segment operates.

Objectives

The overall goal of this research is to investigate improving the properties of three southern hardwoods as feedstock for SCL fabrication. A partial hydrolysis in pressurized, yet relatively low temperature conditions was employed at three pH conditions. By only partially hydrolyzing these woods, easily hydrolyzed substances, such as wood extractives and pentosan hemicelluloses, can be isolated with the modified wood remaining structurally whole. This would first allow for the utilization of wood

sugars for ethanol conversion (Yoon 1998; Garrote and Parajo 2002). Additionally, the cellulose chains of the modified, yet structurally whole, wood material would remain largely intact but with a lower degree of polymerization (Richter 1932; Sjöström 1993). This modified hardwood material may prove to be a superior furnish compared with current raw materials while at the same time providing added value to the ethanol conversion process by effectively utilizing small-diameter underutilized hardwood resources.

The specific objectives of this study were to determine the effect of three treating solutions, 1% sulfuric acid, water, and 1% sodium hydroxide, on three common southern hardwood species, red oak, sweetgum, and yellow-poplar. Untreated controls were also utilized. Response variables investigated following treatment included 1) modulus of elasticity, 2) specific gravity, 3) mass loss due to treatment, 4) surface free energy, and 5) subterranean termite degradation. A chemical analysis (6) was then conducted to relate these response variables to changes in the woods' polysaccharide compositions.

The following chapters of this dissertation are organized by first using 3 mm x 15 mm x 150 mm (t x r x l) miniature beams to quantify mechanical and physical properties. The beams were treated and tested where modulus of elasticity, specific gravity, and mass loss of the wood material. Second, the wetting properties of the treated wood material were characterized by utilizing dynamic contact angle analysis (DCA) of thin wood samples. Surface free energy was then calculated by applying the Geometric Mean procedure. Third, the biological durability of the modified woods was investigated by subjecting them to a 28 day AWPA E1 termite feeding test with four hundred eastern subterranean termites, *Reticulitermes flavipes* Kollar, Termite activity was measured as

mass loss due to termite feeding. Fourth, a chemical component analysis was conducted to find the holocellulose content following the partial hydrolysis treatments. Simple linear regression was then used to relate the changes in the above responses to the changes in total wood sugars.

Literature Cited

Adams DB (2002) Solid wood products: Rising consumption and imports, modest price growth. J Forest 100(2):14-19.

APA – The Engineered Wood Association (2007) Engineered Wood Construction Guide. http://www.apawood.org/pdfs/managed/E30.pdf?CFID=3677399&CFTOKEN=10294707

Bechtold WA (1989) Southern hardwood growth – Use gap closing fast as inventories peak. Pulp Paper, July 79-83.

Beech JC (1975) The thickness swelling of particleboard. Holzforschung. 29(1):11-18.

Blankenhorn PR, Labosky, Jr, P, Stover LR, and Nicholls D (1989) Selected chemical modifications of red oak and hard maple flakes for flakeboard manufacturing. Wood Fiber Sci 21(2):169-176.

Bowyer J (1995) Wood and other raw materials for the 21st century. Forest Prod J 45(2): 17-24.

Birol F (2006) Oil market outlook and policy implications. Prepared testimony before the United States Senate Committee on energy and Natural Resources, January 10, 2006, Washington D.C. 22 pp. www.energy.senate.gov/public/_files/Birol.doc

Carll CG (1996) Review of thickness swell in hardboard siding – Effect of processing variables. Gen Tech Rep FPL-GTR-96. USDA For Serv Forest Products Laboratory, Madison, WI. 10 pp.

Collins K (2006) Economics of biofuels: ethanol and biodiesel. Statement before the United States Senate Committee on Environment and Public Works, September 6, 2006, Washington D.C. 13 pp. http://www.usda.gov/oce/newsroom/congressional_testimony/Biofuels%20Testimony%209-6-2006.doc

Council on Foreign Relations (2006) National security consequences of U.S. oil dependency. Independent task force report no. 58. http://www.cfr.org/content/publications/attachments/EnergyTFR.pdf.

Downing M, McLaughlin S, Walsh M (1995) Energy, economic, and environmental implications of production of grasses as biomass feedstocks. Pages 288-297 *in* Proc Second Biomass Conference of the Americas: Energy, Environment, Agriculture, and Industry, Portland, OR.

FPL (1999) Wood Handbook – Wood as an engineering material. Gen. Tech. Rep. FPL – GTR-113. USDA For Serv Forest Products Laboratory, Madison, WI. 463 pp.

Garrote G, Dominguez H, Parajo JC (1999) Hydrothermal processing of lignocellulosic materials. Holz Roh Werkst 57(1999):191-202.

Garrote G and Parajo J (2002) Non-isothermal autohydrolysis of Eucalyptus wood. Wood Sci Technol 36(2002):111-123.

Halligan AF (1970) A review of thickness swelling in particleboard. Wood Sci Technol 4(4):301-312.

Hamelinck CM, van Hooijdonk G, Faaij APC (2005) Ethanol from lignocellulosic biomass: tecno-economic performance in short-, middle-, and long-term. Biomass Bioenerg 28(2005):384-410.

Hammet AL and Youngs RL (2002) Innovative forest products & processes. Meeting growing demand. J Forest 100(4):6-11.

Harper RA (2004) Softwood timber supply outlook and influences. Presented at Southern Forest Products Association 2004 Annual Meeting, Asheville, NC, September 26-28, 2004. 33 pp.

Hoover WL, Hunt MO, Lattanzi RC, Bateman JH, Youngquist JA (1992) Modeling mechanical properties of single-layer, aligned, mixed-hardwood strand panels. Forest Prod J 42(5):12-18.

Hse CY (1975) Properties of flakeboards from hardwoods growing on southern pine sites. Forest Prod J 25(3):48-53.

ICC Evaluation Service, Inc (2007) ES Report – ESR-1053. www.icc-es.org.

Knudson RM (1992) PSL 300® LSL: The challenge of a new product. Proceedings of the 26th International Particleboard Symposium, Washington State University, Pullman, WA.

McNatt JD and Moody RC (1990) Structural composite lumber. Prog Archit 12.90:34-36.

Nelson S (1997) Structural composite lumber. Pages 147-172 *in* S. Smulski *Engineered Wood Products – A Guide for Specifiers, Designers, and Users*. PFS Research Foundation, Madison, WI.

Paredes JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2009) Influence of hot water extraction on the physical and mechanical behavior of OSB. Forest Prod J 58(12):56-62.

Richter GA (1932) Multistage process of pulping raw cellulosic material. United States Patent Office Patent # 1,880,048. United States Patent Office, Washington D.C.

Schultz TP, Biermann C, McGinnis G (1983) Steam explosion of mixed hardwood chips as a biomass pretreatment. Ind Eng Chem Prod Res Dev 22(2):344-348

Sheffield RM and Bechtold WA (1990) Volume and availability of eastern hardwoods. Pages 55-65 *in* Proc Eighteenth Annual Hardwood Symposium of the Hardwood Research Council, May 1990. Cashiers, NC.

Sheffield RM and Dickson JG (1998) The South's forestland – on the hot seat to provide more. Pages 316-331 *in* Proc Transactions of the 63rd North American Wildlife and Natural Resources conference, 20-25 March 1998, Orlando, FL. Wildlife Management Institute, Washington, DC.

Sjöström E (1993) Wood Chemistry: Fundamentals and applications. Academic Press, San Diego, CA. 293 pp.

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technol 83:1-11.

Thomas RJ (1977) Wood: Structure and chemical composition. Pages 17-23 *in* IS Goldstein *Wood Technology: Chemical Aspects*. American Chemical Society, Washington D.C.

Tolbert M and Schiller A (1996) Environmental enhancement using short-rotation woody crops and perennial grasses as alternatives to traditional agriculture crops. *In* Proc Environmental Enhancement Through Agriculture, Tufts University, Medford, MA.

Yoon HH (1998) Pretreatment of lignocellulosic biomass by autohydrolysis and aqueous ammonia percolation. Korean J Chem 15(6):631-636.

Youngquist JA, Krzysik A, Rowell RM (1986) Dimensional stability of acetylated aspen flakeboard. Wood Fiber Sci 18(1):90-98.

CHAPTER II

BENDING STIFFNESS OF CHEMICALLY TREATED WOOD MATERIAL

Introduction

The products classified as structural composite lumber (SCL) take advantage of wood material processed from small trees and branches that are inadequate for solid-sawn lumber production. The southern United States' current furnish for SCL is primarily southern pine, *Pinus spp.*, though yellow-poplar (*Liriodendron tulipifera* L.), sweetgum (*Liquidambar styraciflua* L.), and red oak (*Quercus spp.*), are readily available. Thus, efforts need to be made to utilize these species for large-scale SCL manufacturing.

Manufacturing constraints due to density and adhesion, among others, currently limit the extensive use of hardwoods in wood composite manufacturing (Hse 1975). It has been found during pressing that lower density species are compressed more than higher density species due to thinner cell walls (Halligan 1970). Swelling due to springback, which weakens the wood-adhesive bond, is minimized at an appropriate compaction ratio (Caril 1996). Higher compaction ratios result in more efficient adhesive distribution and penetration (Larmore 1959). Modification of hardwoods by treating with heat, chemicals, or a combination thereof, can potentially overcome manufacturing and service limitations (Paredes et al. 2009; Youngquist et al. 1986). This chapter reports the initial results of partially hydrolyzing miniature beams in pressurized, high temperature

conditions by determining the effect of a chemical treatment on reducing the stiffness of solid wood material.

Experimental

Design

Yellow-poplar, sweetgum, and red oak specimens were treated in a 2 L reactor at 150°C for 30 minutes and tested by static bending. Three solutions were utilized: 1.0% sulfuric acid (H_2SO_4), water (H_2O), and 1.0% sodium hydroxide (NaOH). Six replications were performed with the experimental unit being one beam (n=54). Specimens were tested both before and after extraction, resulting in a matched sample to determine the percent change in MOE. Thus, the difference between the pre-treatment and post-treatment responses could be attributed to the changes caused by the solution, and not to the differences among the samples. Each replication was performed daily for blocking purposes to control for variation due to laboratory conditions. A randomized complete block design (RCB) was constructed using the model

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \delta_k + e_{ijk} \qquad (2.1)$$
$$\text{where } \delta_k \sim N(0, \sigma_\delta^2), \text{ iid}^{a} \text{ and } e_{ijk} \sim N(0, \sigma^2), \text{ iid} \Big\} \text{ Ind.}^{b}$$

where $\alpha_{i\ (i = 1, 2, \ldots, a)}$ represented the main effect due to Factor A [Species], $\beta_{j\ (j = 1, 2, \ldots, b)}$ represented the main effect due to Factor B [Solution], $(\alpha\beta)_{ij}$ represented the interaction

[a] Independent and identically distributed
[b] Independent

of Factors A and B [Species x Solution], $\delta_{k\ (k = 1, 2, ..., r)}$ represented the block [Day], and e_{ijk} represented the error of the model.

The following hypotheses were tested:

- Block: Did the days vary relative to the response?
- Factor A: Did the species perform equally relative to the response?
- Factor B: Did the treating solutions perform equally relative to the response?
- Factor A x B: Was the response to the treating solution equal across the species?

Materials

Rough-cut red oak, sweetgum, and yellow-poplar lumber, 50 mm x 292 mm x 2.44 m, was obtained from a local sawmill. The red oak and sweetgum lumber had been freshly sawn within the previous day, while the yellow-poplar had been air-drying for some time. Care was taken to select boards free of sawing and drying defects. The lumber was stored at 2°C.

For this initial study, one board was randomly selected from each species to create the experimental samples to minimize sample variation. The specimens were processed and tested following the principles described in AWPA Standard Method E23 (AWPA 2008). The board was ripped and then sawn into strips measuring 3 mm x 15 mm x 150 mm (t x r x l). The samples were returned to the 2°C room for four weeks before being conditioned, measured, and tested.

Methods

The samples were saturated in deionized water at 85 kPa to achieve full saturation. After setting for one hour, the length, width, thickness, and mass were recorded. Static bending was performed utilizing a 45 N load cell on a bending machine designed to be used for small three-point bending tests of preservative treated samples. The specimens were placed at room temperature for four hours prior to bending and tested to a deflection of 1.0 mm (Figure 2.1). The MOE was then determined. This was repeated three times with at least 24 hours in between each test. The value of the third test served as the initial MOE as stated by AWPA E-23.

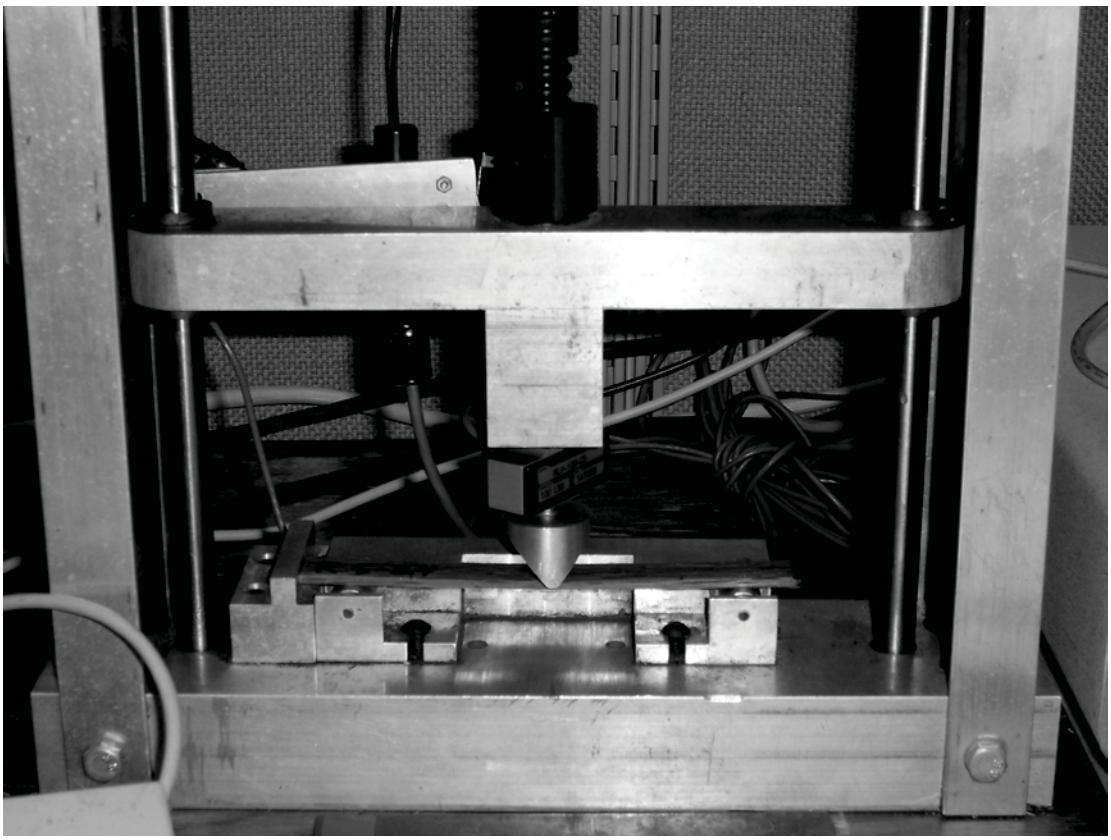

Figure 2.1

Three point bending machine.

Chemical treatment was conducted using a Parr 4843 2 L reactor. The vessel was filled with 1700 mL of solution and a miniature beam was immersed for the designated treatment combination. Time measurement began at the point in which the reactor reached 150°C. After treatment, the specimen was washed, and then placed in a bath of deionized water for 24 hours. A blank run of only the next solution with no wood was conducted between treatments to thoroughly clean the vessel and prevent contamination by the previous species/solution combination. The samples were stored for one week, then measured and tested to determine the post-extraction MOE. The change in MOE was calculated. Results were analyzed using analysis of variance (ANOVA) with a 0.05 level of significance. Multiple comparisons were made using Fisher's protected least significant difference in SAS 9.1.3 (2003).

Results and Discussion

Average pH values were 3.5, 6.5, and 10 for the H_2SO_4, water, and NaOH solutions, respectively. After treatment, the acid solutions were emerald-green, and the alkaline solutions were reddish-brown likely due to some lignin being removed in these solutions (Hagglund 1951). The water solutions were amber. The species and treatment solutions interacted to significantly affect the mean reduction in MOE ($p = 0.0212$). The trend in mean response was generally a quadratic function of the solution for each species ($p = 0.0036$).

The results of the multiple comparisons in Table 2.1 indicated that some of the treatments were significantly different, notably the acid and alkaline solutions when compared to the water solutions. The acidic and basic solutions consistently reduced the

mean MOE when compared to water. Sweetgum produced a higher reduction in MOE in all three solutions, being significantly greater in the alkaline solution. Yellow-poplar produced the least significant decrease in both the acid and water solutions.

Table 2.1

Least significant difference (LSD) results for the treatment means based on six observations. Means with the same capital letter were not significantly different at $\alpha = 0.05$. LSD = 8.07 GPa.

Treatment	Reduction in MOE, %	t Grouping
Sweetgum/NaOH	-65.21	A
Sweetgum/H_2SO_4	-60.25	AB
Red Oak/H_2SO_4	-58.50	ABC
Yellow-poplar/NaOH	-56.98	BC
Red Oak/NaOH	-51.33	CD
Yellow-poplar/H_2SO_4	-46.35	D
Sweetgum/Water	-2.21	E
Red Oak/Water	0.08	E
Yellow-poplar/Water	11.71	F

Overall, treating with water produced the least significant loss in bending stiffness. In fact, results differed between species as mean stiffness decreased overall for sweetgum while increasing for yellow-poplar. Red oak showed virtually no change. When wood is first heated under moist conditions, MOE initially increases slightly. A subsequent reduction follows upon higher heating times and/or temperatures (Mitchell

1988). Differences in reactivity between species can also produce varying effects within the same treatment (Rowell et al. 1986). Larsson and Simonson (1994) reported such results when Scots pine and Norway spruce underwent acetylation followed by a thermal treatment. They found that MOE decreased for pine and increased for spruce. Bongers and Beckers (2003) found that while mechanical properties varied between species after a chemical treatment, they were consistent within a species. In this research, a water treatment provided inconsistent results within both sweetgum and red oak.

Conclusions

The effect of a chemical treatment on the bending stiffness of three southern hardwoods was studied. Water produced the least significant reduction in MOE for each species. While water would be the most economical, higher temperatures, longer treatment times, or a combination thereof will need to be further researched to attain comparative results with an acidic or alkaline treatment.

Literature Cited

AWPA (2008) Accelerated method of evaluating wood preservatives in soil contact. E-23-07. American Wood Protection Association, Birmingham, AL.

Bongers HPM, Beckers EPJ (2003) Mechanical properties of acetylated solid wood treated on pilot plant scale. Page 59 *in* Callum Hill Wood Modification - Chemical, Thermal, and other Processes. John Wiley & Sons, West Sussex, England.

Carll CG (1996) Review of thickness swell in hardboard siding – Effect of processing variables. Gen Tech Rep FPL-GTR-96 USDA Forest Prod Lab, Madison, WI.

Hagglund E (1951) Chemistry of Wood. Academic Press, New York. 631 pp.

Halligan AF (1970) A review of thickness swelling in particleboard. Wood Sci Technol 4(4):301-312.

Hse CY (1975) Properties of flakeboards from hardwoods growing on southern pine sites. Forest Prod J 25(3):48-53.

Larmore FD (1959) Influence of specific gravity and resin content on properties of particleboard. Forest Prod J 9(4):131-134.

Larsson P, Simonson R (1994) A study of the strength, hardness, and deformation of acetylated Scandanavian softwoods. Page 59 *in* Callum Hill Wood Modification - Chemical, Thermal, and other Processes. John Wiley & Sons, West Sussex, England.

Mitchell PH (1988) Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen. Wood Fiber Sci 20(3):320-355.

Paredes JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2009) Influence of hot water extraction on the physical and mechanical behavior of OSB. Forest Prod J 58(12):56-62.

Rowell RM, Tillman A-M, Simonson R (1986) A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. J Wood Chem 6(3):427-448.

SAS (2003) SAS Institute. Version 9.1.3. Cary, NC.

Youngquist JA, Krzysik A, Rowell RM (1986) Dimensional stability of acetylated aspen flakeboard. Wood Fiber Sci 18(1):90-98.

CHAPTER III

EFFECTS OF A PARTIAL HYDROLYSIS ON THE MODULUS AND MASS LOSS OF THREE SOUTHERN HARDWOODS

Introduction

The wood composite market in the southeastern United States is primarily limited to southern yellow pine (*Pinus spp*.), which is intensively managed throughout the region. Strand-based composite mills are largely supplied by plantation first thinnings. However, the South is also a major hardwood region with species, such as red oak (*Quercus* spp.), sweetgum (*Liquidambar* styraciflua L.), and yellow-poplar (*Liriodendron* tulipifera L.) readily available in small diameter classes (Sheffield and Bechtold 1990). In fact, sweetgum is the most populous hardwood species growing on southern pine sites in the South (Koch 1985).

These species are currently used on a limited basis due to various wood properties which adversely affect the composite's product quality. For example, thicker cell walls in red oak can prevent adequate adhesive penetration while the heartwood of sweetgum is generally impermeable as abundant phenolic glycosides are polymerized (Halligan 1970; Rowe and Connor 1979). Acidic extractives can gel PF resin while alkaline extractives can deactivate UF resin (Beech 1975). These factors, along with variations in density, lead to inefficient compaction ratios for composites of mixed species, which weaken the wood-adhesive bond due to springback (Carll 1997). Hse (1975) evaluated nine

hardwoods that commonly grow on southern pine sites and found only three produced adequate panels, sweetbay (*Magnolia virginia* L.), red maple (*Acer rubrum* L.), and sweetgum. Sweetgum required the highest compaction ratio tested to meet minimum requirements. Biblis (1985) constructed two blends of three-layer oriented strandboard (OSB) from a mixture of southern hardwoods. Results varied as flexural properties were lower when compared with the published values of southern pine plywood and aspen flakeboard, but shear properties were improved.

One branch of research is focused on the hydrolyzing and utilization of easily extracted wood components, such as pentosan hemicelluloses from hardwoods (Richter 1932). The use of wood sugar molasses as livestock feed supplement, for instance, dates to World War I (Colovos et al. 1949). In recent years energy independence has led investigators to examine various pretreatments of hardwood species for conversion of wood sugars to ethanol (Sun and Cheng 2002). These studies utilized small-diameter trees that otherwise would have little or no market value. Many of the processes result in the complete hydrolysis of the polysaccharides, leaving behind the lignin that is primarily burned for energy (Garrote and Parajo 2002). Conversely, it may be possible to conduct only a partial hydrolysis pretreatment on the woody material, forming some hydrolyzed sugars to ferment but also leaving behind a partially modified wood substrate. Linking pulp and paper manufacturing to biofuel production has been reviewed, but few studies have been conducted on wood properties following treatment in a heated solution (Ragauskas et al. 2006; Hill 2006). Modified wood material from previously unusable hardwood resources may possess improved properties for producing strand-based wood composites.

A partial hydrolysis pretreatment would employ relatively low temperatures and/or chemical concentrations; therefore, the wood remains structurally whole rather than being pulped to individual fibers. This may lead to a reduction in stiffness, which, in turn, could lead to improved compaction during pressing. The hemicelluloses are most susceptible to hydrolysis and subsequent extraction followed by some lignin while cellulose's degree of polymerization (DP) is lowered (Connor 1984). An overall decrease in mechanical properties usually occurs with increased treatment time and changes in chemical composition (Thompson 1969; Winandy and Lebow 2001). Wangaard (1966) investigated the chemical degradation of several softwoods and hardwoods and found strength retention was higher when wood was exposed to an acid versus an alkaline treatment. Producing OSB from red maple strands hydrolyzed in water with different severity factors was investigated (Paredes et al. 2008; Howell et al. 2009; Mills et al. 2009; Paredes et al. 2009). These studies found that most hemicelluloses could be removed and, at the same time, the wettability of the wood was improved. Mechanical, physical, and durability properties were maintained or improved.

Partially hydrolyzing hardwood furnish not only allows for the utilization of hemicelluloses for ethanol conversion but also fosters a value-added composite product from small-diameter underutilized hardwood resources. The goals of this chapter were to understand the effects of three partial hydrolysis treatments on red oak, sweetgum, and yellow-poplar miniature beams in pressurized, heated conditions. The influence of the species and treatments on modulus of elasticity (MOE), density, and mass loss (ML) were investigated.

Experimental

Design

Red oak, sweetgum, and yellow-poplar specimens were treated in a 2 L reactor at 150°C for 30 min, dried, then weighed and tested in static bending. Three solutions, 1.0% sulfuric acid (H_2SO_4), water, 1.0% sodium hydroxide (NaOH), along with untreated controls were utilized. The MOE (GPa), oven-dry density (g/cm^3), and ML (%) were then determined. Six replications were performed for the 12 treatment combinations (n=72), and the experimental unit was one beam. Static bending followed AWPA Standard E23 (2009) while ML was determined by the methods described in AWPA Standard E1 (2009). A completely randomized (CR) design was constructed using the model

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + e_{ijk} \quad (3.1)$$
$$\text{where } e_{ijk} \sim N(0, \sigma^2), \text{ iid}$$

where $\alpha_{i\ (i = 1, 2, ..., a)}$ represented the main effect due to Factor A [Species], $\beta_{j\ (j = 1, 2, ..., b)}$ represented the main effect due to Factor B [Solution], $(\alpha\beta)_{ij}$ represented the interaction of Factors A and B [Species x Solution], and e_{ijk} represented the error of the model.

The following hypotheses were tested:

- Factor A: Did the species perform equally relative to the response?
- Factor B: Did the treating solutions perform equally relative to the response?
- Factor A x B: Was the response due to the solution equal across the species?

Materials

Rough-cut red oak, sweetgum, and yellow-poplar lumber was obtained from a local sawmill. The red oak and sweetgum lumber had been freshly sawn within the previous day while the yellow-poplar had air-dried for some time. The rough lumber size was 50 mm thick by 292 mm wide by 2.44 m long. Care was taken to select wood free of sawing and drying defects. The selection of boards was randomized. Five boards from each species were selected. The lumber was stored at 2°C.

One board was randomly selected from each species for further processing to minimize sample variation. The board was ripped into six pieces sized 50 mm by 76 mm by 813 mm. The pieces were then sawn into strips measuring 3 x 15 x 150 mm (t x r x l). The prepared samples were then sealed in plastic bags and returned to the 2°C room.

Methods

The initial moisture content (MC) was calculated from a subset and averaged for each species. Eighteen samples from each species were selected to determine the initial moisture content. Samples (n=54) were oven-dried at 103 ± 3°C for 24 hours. Using the initial MC of the lumber, the oven-dry weights of the test samples were then estimated.

All samples were saturated in deionized water under a vacuum pressure of 85 kPa to achieve full saturation. Chemical treatment with 1% H_2SO_4, water and 1% NaOH was conducted using a Parr 4843 2-L pressure reactor. The vessel was filled with 1,700 mL of solution and a miniature beam was immersed. Glass fiber was placed over the wood sample as a weight to ensure full immersion in the liquid. Time measurement began at the point in which the reactor reached 150°C. After 30 minutes had elapsed the vessel

was cooled and the pressure then released. The specimen was washed with deionized water and placed in a bath of deionized water for 24 hours. The reactor was thoroughly cleaned after each run. A blank run of only the next solution, with no wood, was conducted between treatments to prevent contamination by the previous species/solution combination.

The samples were allowed to rest in storage for one week. The moisture content of the miniature beams was then gradually reduced downward to minimize sample distortion. They were first put in a dehumidification chamber at a temperature of 20 ± 3°C and a relative humidity of 65 ± 5% until a constant weight was achieved. They were next placed in a convection oven at 60°C until attaining a constant weight, then dimensionally measured, weighed, and tested in static bending per AWPA E23 (AWPA 2009). Static bending utilized a 45 N load cell on a bending machine designed to be used for small three-point bending tests of preservative treated samples. The specimens were tested to a maximum deflection of 1.0 mm. The loading speed was 10 to 20 mm/minute, the loading span was 120 mm, and span-to-depth ratio was 40. The stress/strain data obtained was used to calculate the MOE for each sample. The oven-dry density was determined. The ML was calculated as the percentage (%) change in dry mass at the end of the test. Results were analyzed using analysis of variance (ANOVA) with an alpha = 0.05 level of significance. Multiple comparisons were made using Fisher's protected least significant difference in SAS 9.1.3 (2003).

Results and Discussion

Summary statistics are presented in Table 3.1 for MOE and oven-dry density [mass and volume both at oven-dry condition]. Initial moisture contents were 55.6%, 44.8%, and 20.1% for the red oak, sweetgum, and yellow-poplar respectively. Treatment pH averaged 3.5 for the H_2SO_4, 6.5 for the water, and 10.0 for NaOH.

Table 3.1

Average MOE and oven-dry density (standard deviation).

Species	Treatment	MOE (GPa)	Density (g/cm^3)
Oak	H_2SO_4	13.44 (1.52)	0.72 (0.06)
	Water	19.05 (1.54)	0.76 (0.01)
	NaOH	20.49 (3.08)	0.87 (0.09)
	Control	17.50 (0.67)	0.69 (0.01)
Sweetgum	H_2SO_4	8.73 (3.26)	0.58 (0.04)
	Water	10.94 (3.81)	0.68 (0.03)
	NaOH	12.23 (3.34)	0.71 (0.04)
	Control	11.47 (2.57)	0.67 (0.03
Yellow-poplar	H_2SO_4	9.54 (1.51)	0.35 (0.03)
	Water	9.78 (0.76)	0.40 (0.01)
	NaOH	9.53 (1.45)	0.48 (0.02)
	Control	10.31 (1.15)	0.41 (0.02)

Modulus

Wood properties are well known to vary widely between species (e.g. Panshin and de Zeeuw 1980). Mechanical properties are generally dependent upon the density; for instance, the higher the density, the greater the MOE (Haygreen and Bowyer 1996). Moreover, density can vary not only between and within a species, but also within a single tree (Sjöström 1993).

There were many inherent differences between the species and the solvents chosen for this experiment. Accounting for the density variation both between and within the species in addition to any wood-treatment interactions allowed for higher accuracy when comparing mechanical properties (Sun and Hawke 1997). Thus, specific modulus (SM) was utilized for property comparisons to eliminate the density effect (Shi and Gardner 1999). It is expressed as

$$SM = \frac{S}{SG} \tag{3.2}$$

where SM is the specific modulus, S is the modulus of elasticity (MOE), and SG is the specific gravity of the wood specimen at the designated moisture content, which is equal to the sample density since both weight and volume are oven-dry basis.

The effect of the treating solution on SM was species-specific (Table 3.2) as the interaction between the two factors was significant ($p = 0.0027$). Red oak SM was consistently reduced by the treatments, with the acid treatment being the least. While no treatment was different for sweetgum, the acid and water treatments were lower than the control. Treating yellow-poplar in a caustic solution significantly decreased SM over the other treatments. Though similar to the controls for all species, water was the only treatment that consistently lowered SM. Prior work on the initial effect of chemically treating wood found a larger reduction in MOE for sweetgum versus the other species (McConnell et al. 2009). A similar effect was observed in this study, in which sweetgum SM was lower than the other species in all treatments, being significantly less in water.

Table 3.2

Least significant difference (LSD) results for the Specific Modulus treatment means (standard deviation) for six observations. Means with the same capital letter were not significantly different at $\alpha = 0.05$. LSD = 4.04 GPa.

Treatment	Specific Modulus (GPa)	t Grouping
Yellow-poplar/H_2SO_4	27.15 (2.76)	A
Red Oak/Control	25.27 (0.70)	A
Yellow-poplar/Control	25.12 (2.30)	A
Red Oak/Water	25.05 (1.81)	A
Yellow-poplar/Water	24.61 (2.04)	A
Red Oak/NaOH	23.58 (2.86)	AB
Yellow-poplar/NaOH	20.02 (3.55)	BC
Red Oak/H_2SO_4	18.69 (1.35)	CD
Sweetgum/NaOH	17.30 (4.46)	CD
Sweetgum/Control	17.18 (4.81)	CD
Sweetgum/Water	16.34 (6.24)	CD
Sweetgum/H_2SO_4	14.77 (4.68)	D

Treatment effects depend in large part upon the species, as varying results can be produced within the same treatment (Rowell et al. 1986). Wood structure, chemical composition, and mechanics all contribute. This experiment found SM results were inconsistent within both the acid and base solutions. The SM for red oak decreased after both acid and base treatments compared to the control specimens. The alkaline treatments increased the SM for sweetgum, and the acid treatment increased the SM for yellow-poplar. The alkaline treatment increased the density for each species, while the acid treatment consistently lowered the density. The water treatment, with the exception of red oak, did not affect the density of the other two species.

Heating wood in alkaline solutions is known to lower cellulose degree of polymerization (DP) through peeling reactions and random scission (Sjöström 1993).

Treating wood in acid quickens the decrease in cellulose DP (Winandy and Lebow 2001). NaOH originally bulks the cell wall before collapsing upon drying, thereby reducing void content and increasing bulk density, while acid makes the wood brash and friable (Wangaard 1966). Heating wood in water at 150°C lowers the pH by cleaving acetyl groups, which decreases the cellulose chain's DP as a result of some autohydrolysis (Connor 1984). These differing effects were eliminated through usage of SM, though inconsistencies across both the species and the treatments were still present.

Mass Loss

Each factor, species and treatment, independently and significantly affected mean ML with the treating solution being the more significant of the two (treatment, $p < 0.0001$; species, $p = 0.0004$). Sweetgum averaged a significantly higher overall ML than the other species, and all treatments resulted in statistically significant ML with the acid treatment producing the highest (Tables 3.3 and 3.4). The controls exhibited very minor ML due to water saturation and subsequent oven-drying.

Table 3.3

Least significant difference (LSD) results for the species mass loss means. Means with the same capital letter were not significantly different at $\alpha = 0.05$. LSD = 2.02%.

Species	Mass Loss, %	t Grouping	Observations
Sweetgum	-17.00	A	18
Yellow-poplar	-14.57	B	18
Red Oak	-12.75	B	18

Table 3.4

Least significant difference (LSD) results for the treatment mass loss means. Means with the same capital letter were not significantly different at $\alpha = 0.05$. LSD = 2.33%.

Treatment	Mass Loss, %	t Grouping	Observations
H_2SO_4	-35.53	A	18
NaOH	-18.47	B	18
Water	-3.85	C	18
Control	-1.24	D	18

As wood is heated in water nonstructural extractives are first removed. A loss in DP of the polysaccharides through autohydrolysis follows, with some degraded polysaccharide-derived compounds becoming water-soluble, via the production of and subsequent reactions with acetic acid (Rowell 1984; Mitchell 1988). The presence of an acid or caustic can accelerate this deterioration, with acid being the more severe (Kass et al. 1970; Hill 2006). The caustic solution also likely affects the lignin while the acid treatment likely causes further degradation of the sugars to form furans, a portion of which can condense to form a pseudo-lignin (Schultz 2010). Further, pentosan content and wood degradation are directly related to one another (Kass et al. 1970). Hergert et al. (1985) reported that sweetgum possessed higher cellulose and hemicellulose contents than red oak or yellow-poplar, which may explain the results obtained in this study.

Conclusions

Specific modulus was calculated for bending comparisons to eliminate the density variations. The SM was both species- and treatment-dependent. Red oak SM was consistently reduced by the treatments. No treatments were significantly different for

sweetgum. Treating wood by a partial hydrolysis in solution resulted in statistically significant ML. Utilizing an acid treatment produced the greatest treatment effect on ML. Future research will investigate utilizing sweetgum as the primary species in a mixed furnish of water-treated partially hydrolyzed hardwood flakes. In this study sweetgum's ML was significantly greater than the other species, and water treatments lowered SM for all species. Moreover, SM was lower for sweetgum versus the other species in each treatment, being significantly so in water.

Literature Cited

American Wood Protection Association (2009) AWPA Book of Standards. AWPA, Birmingham, AL.

Beech J. (1975) The thickness swelling of particleboard. Holzforschung 29(1):11-18.

Biblis E (1985) Properties of three-layer strandboard from southern hardwoods. Forest Prod J 35(2):28-32.

Carll C (1997) Review of thickness swell in hardboard siding – Effect of processing variables. USDA Forest Products Laboratory GTR-96. 10 pp. http://www.fpl.fs.fed.us/documnts/fplgtr/fplgtr96.pdf.

Colovos N, Keener H, Prescott J, Teeri A (1949) The nutritive value of wood molasses as compared with cane molasses. J Dairy Sci 32(11):907-913.

Connor A (1984) Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood Fiber Sci 16(2):268-277.

Garrote G, Parajo J (2002) Non-isothermal autohydrolysis of Eucalyptus wood. Wood Sci Tech 36:111-123.

Halligan A (1970) A review of thickness swelling in particleboard. Wood Sci Tech 4(4):301-312.

Haygreen J, Bowyer J (1996) Forest Products and Wood Science. An Introduction. Third Edition. Iowa State University Press. Ames, IA. 484 pp.

Hergert H., Sloan T, Gray J, Sandberg K (1977) The chemical composition of southeast hardwoods. *In* Peter Koch Utilization of Southern Hardwoods Growing on Southern Pine Sites. United States Department of Agriculture Forest Service Agriculture Handbook, United States Government Printing Office, Washington D.C. p. 368.

Hill C (2006) Wood Modification. Chemical, Thermal and Other Processes. Wiley & Sons, Sussex, England. 239 pp.

Howell C, Paredes J, Jellison J (2009) Decay resistance properties of hot water extracted oriented strandboard. Wood Fiber Sci 41(2):201-208.

Hse C (1975) Properties of flakeboards from hardwoods growing on southern pine sites. Forest Prod J 25(3): 48-53.

Kass A, Wangaard F, Schroeder H (1970) Chemical degradation of wood: The relationship between strength retention and pentosan content. Wood Fiber Sci 2(1):31-39.

Koch P (1985) Utilization of hardwoods growing on southern pine sites. Volume I: The raw material. United States Department of Agriculture Forest Service Agriculture Handbook, United States Government Printing Office, Washington D.C. 1418 pp.

McConnell TE, Shi SQ, Shmulsky R (2009) A preliminary study on the bending stiffness of chemically treated wood material for structural composite lumber. Wood Fiber Sci 41(3):322-324.

Mills R., Jara J, Gardner D, van Heiningen A (2009) Inverse gas chromatography for determining the surface free energy and acid-base chemical charactristics of a water extracted hardwood (*Acer rubrum*). J Wood Chem 29:11-23.

Mitchell P (1988) Irreversible property changes of small loblolly pine specimens heated in air, nitrogen, or oxygen. Wood Fiber Sci 20(3):320-355.

Panshin A, de Zeeuw C (1980) Textbook of Wood Technology: Structure, Identification, Properties, and Uses of the Commercial Woods of the United States and Canada. Fourth Edition. McGraw-Hill, Inc., New York. 722 pp.

Paredes J, Mills R, Shaler S, Gardner D, van Heiningen A (2008) Influence of hot water extraction on the physical and mechanical behavior of OSB. Forest Prod J 58(12):56-62.

Paredes J, Mills R, Shaler S, Gardner D, van Heiningen A (2009) Surface characterization of red maple strands after hot water extraction. Wood Fiber Sci 41(1):38-50.

Ragauskas A, Nagy M, Kim D, Eckert C, Hallett J, Liotta C (2006) From wood to fuels: Integrating biofuels and pulp production. Ind Biotechnol 12(1):55-65.

Richter G (1932) Multistage process of pulping raw cellulosic material. United States Patent Office Patent # 1,880,048. United States Patent Office, Washington D.C.

Rowe J, Connor A (1979) Extractives in eastern hardwoods. USDA Forest Products Laboratory GTR-18. 72 pp.

Rowell R (1984) The Chemistry of Solid Wood. American Chemical Society, Washington DC. 614 pp.

Rowell R, Tillman A, Simonson R (1986) A simplified procedure for the acetylation of hardwood and softwood flakes for flakeboard production. J Wood Chem 6(3):427-448.

SAS Institute (2003) Version 9.1.3. SAS Institute, Cary, NC.

Schultz T (2010) Mississippi State University. Personal communication. Forest Prod. Lab., Mississippi State, Miss. February.

Sheffield R, Bechtold W (1990) Volume and availability of eastern hardwoods. *In*: Proc. Eighteenth Annual Hardwood Symposium of the Hardwood Research Council. Cashiers, North Carolina. pp. 55-65

Shi SQ, Gardner DJ (1999) An evaluation of analysis methods to eliminate the effect of density variation in property comparisons of wood composites. Wood Fiber Sci 31(2):164-172.

Sjöström E (1993) Wood Chemistry: Fundamentals and applications. Academic Press, San Diego, CA. 293 pp.

Sun B, Hawke R (1997) Properties of polyisocyanate resin consolidated composites made from secondary fibers of corrugated containers. Forest Prod J 47(2):80-88.

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: A review. Bioresour Technol 83(2002):1-11.

Thompson WS (1969) Effect of steaming and kiln drying on the properties of southern pine poles. Part II: Chemical properties. Forest Prod J 19(2):37-43.

Wangaard F (1966) Resistance of wood to chemical degradation. Forest Prod J 16(2):53-64.

Winandy J, Lebow P (2001) Modeling strength loss in wood by chemical composition . Part I. An individual component model for southern pine. Wood Fiber Sci 33(2):239-254.

CHAPTER IV

WETTABILITY OF PARTIALLY HYDROLYZED HARDWOODS DETERMINED BY DYNAMIC CONTACT ANGLE ANALYSIS

Introduction

The primary timber source for strand-based wood composites in the southern United States is southern pine (*Pinus spp.*), but the increasing demand for composite products is straining this feedstock supply. Hardwoods, such as yellow-poplar, (*Liriodendron tulipifera* L.), sweetgum, (*Liquidambar styraciflua* L.), and red oak, (*Quercus spp.*), associate with pines on sites across the region, are plentiful, and inexpensive. However, the extractives in these species, such as resin, carbohydrate metabolites, etc., affect their adhesion performance (Chen 1968). These extractives are generally of low molecular weight and independent of the lignocellulosic structure. Migration of these nonstructural components onto the wood surface contributes to surface deactivation, compromising the wood-adhesive bond during pressing (Parham and Gray 1984; Thomas 1977). Oak, for example, prematurely gels phenol formaldehyde (PF) resin due to the release of acidic extractives (Beech 1975). Utilizing mixed hardwood furnish also results in a lower compaction ratio, the panel to wood species density, which can lead to venting issues during the press cycle. This is due to low density species being compressed more than high density species at the same pressure. Thinner cell walls and greater lumen volumes contribute to less pressing resistance (Halligan 1970). Low

compressive pressures result when pressing high-density hardwoods, with extractives content and hardwood density directly related (Carll 1996).

Modifying wood by chemical processes dates back decades with large scale processing beginning during World War II in Germany. Following the war, the Americans improved upon the technology for the livestock industry (Gilbert et al. 1952). In recent years, wood sugar separation has been the focus for alternative fuel production. The utilization of existing infrastructure within the forest products industry to convert small-diameter hardwood species into ethanol has been reviewed (Ragauskas et al. 2006). Many separation processes have been investigated, including acid and alkaline hydrolysis, autohydrolysis, and steam explosion (Schultz et al. 1983; Son and Cheng 2002; Yoon 1998). A biorefinery in the classical sense, though, requires harsh conditions at high temperatures, resulting in the complete breakdown of the wood material into its rudimentary carbohydrate components for sugar harvesting and chemical separation (Fernando et al. 2006). However, performing a less severe treatment at lower temperatures may only partially hydrolyze the wood, removing the extractives followed by easily extracted structural components, such as pentosan hemicelluloses, for fuel conversion while leaving the residual material structurally whole. The modified wood material may demonstrate improved wetting for manufacturing strand-based wood composites.

Past research has shown that treating wood with heat and chemicals affects wetting. The interactions of PF resin and southern yellow pine were investigated (Haupt and Sellers, Jr. 1994). One test involved treating pine with 1% cetyl alcohol in methanol and a PF resin of low surface tension (γ = 53.4 mN/m) in methanol. A PF resin treatment

lowered the contact angle as compared to a control while an alcohol treatment increased the contact angle due to hydrogen bonding with the hydroxyl groups of the cellulose chain. Springwood had greater wetting potential than summerwood. Paredes et al. (2009) investigated the surface properties of red maple following hot water extractions at 160°C for 0, 45, and 90 minutes. Contact angles were determined in water, ethylene glycol, and diiodomethane. Specimens treated for at least 45 minutes showed a 0° contact angle in each probe liquid, resulting in increased surface energies. The longer treatment times resulted in greater removal of both extractives and hemicelluloses, thus increasing the acid/base characteristics of the wood. The basic characteristic showed its largest value at the lowest treatment time, decreasing with time as acetyls were cleaved from the hemicelluloses.

The determining factor for the quality of wood composites is the wood – adhesive bond (Bryant 1968). For wood adhesion to be successful, the adhesive must adequately wet the wood surface. Penetration into the micropore structures of the wood cell wall provides intimate contact between the two wood elements at the molecular level, which is critical for adhesive bonding strength and the product's durability (Nearn 1974). Producing higher compaction ratios results in more efficient wood contact and adhesive distribution as more penetration would increase bond effectiveness between the wood and adhesive (Larmore 1959). Further, swelling due to springback, which weakens the wood-adhesive bond, would be minimized (Carll 1996).

The goals of this study were to determine the dynamic contact angles of miniature beams of three species, red oak, sweetgum, and yellow-poplar after partial hydrolysis. The Wilhelmy plate technique was utilized with four probe liquids. The surface energies

of the treated woods were then calculated by the geometric mean procedure and compared with untreated controls.

Experimental

Materials

Rough-cut red oak, sweetgum, and yellow-poplar lumber was obtained from a local sawmill. The rough lumber size was 50 mm thick by 292 mm wide by 2.44 m long. Care was taken to select wood free of sawing and drying defects. Five boards free of any visual defects were randomly selected and stored at a target temperature of 2°C.

One board was randomly selected from each species to minimize sample variation and further processed into strips measuring 3 mm x 15 mm x 150 mm (t x r x l). All strips were fully saturated in deionized water under vacuum pressure at 85 kPa. Chemical treatment with 1% sulfuric acid (H_2SO_4), water, and 1% sodium hydroxide (NaOH) was conducted using a Parr 4843 2-L Pressure Reactor. The vessel was filled with 1,700 mL of solution, and a miniature beam was immersed. Glass fiber was placed over the miniature beam sample as a weight to ensure full immersion in the liquid. Time measurement began at the point in which the reactor reached 150°C. After 30 minutes had elapsed the vessel was cooled, and the pressure was then released. Each miniature beam was washed with deionized water and placed in a bath of distilled water for 24 hours. The reactor was thoroughly cleaned after each run. A blank run of only the next solution, with no wood, was conducted between treatments to prevent contamination by the previous species/solution combination. Six replicates per treatment combination were performed (3 species x 4 treatments x 6 replicates, n=72).

Following treatment, the miniature beams were placed in a conditioning chamber at 21 ± 2°C and 41 ± 5% relative humidity until attaining a constant weight. Dynamic contact angle samples were planed from the miniature beams with a Stanley No. 90 FJ bullnose plane to a target thickness of 0.25 mm and cut to a target length of 15 mm (r x l). The width (t) varied among the species and the treatments due to the partial hydrolysis. (Figure 4.1).

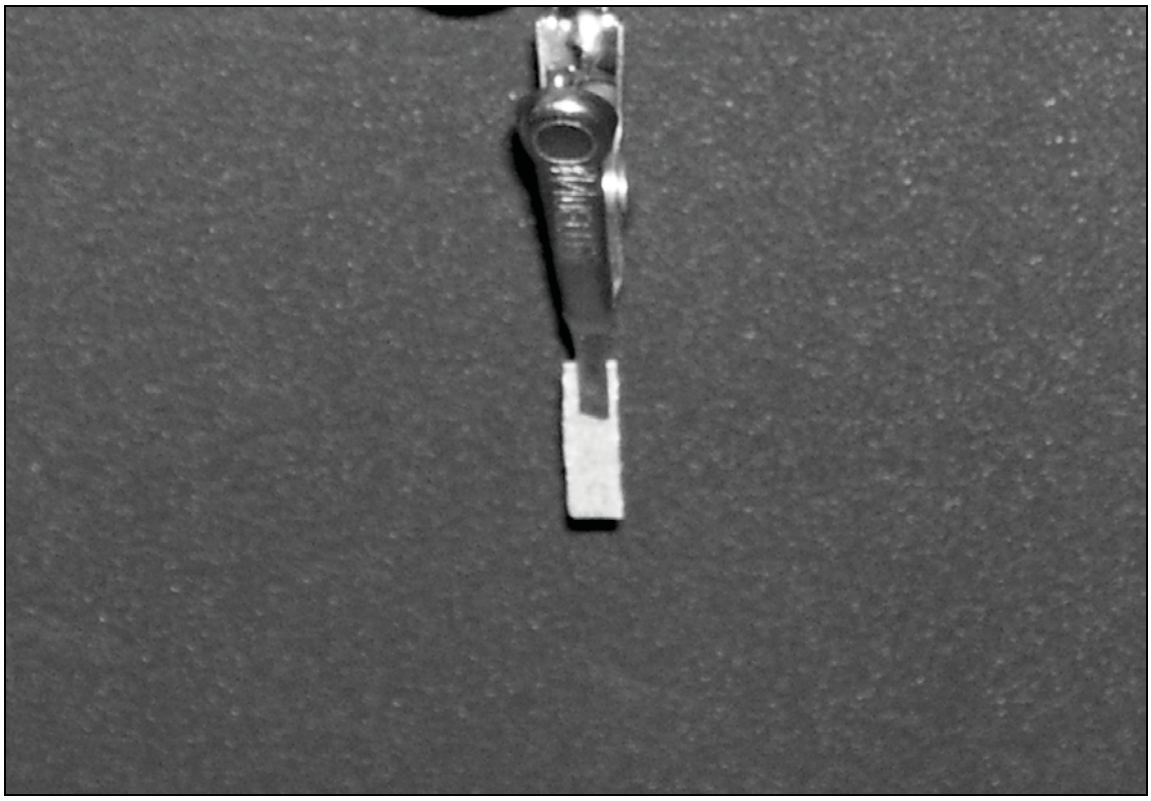

Figure 4.1

Dynamic contact angle sample.

Methods

Contact angle and surface free energy are usually used to evaluate the wettability of materials (Gray 1962). Their relationship was originally described by Young's (1805) equation

$$\gamma_S - \gamma_{SL} = \gamma_l * COS\theta \tag{4.1}$$

where γ_S represents the surface free energy of the solid's surface tension, γ_{SL} represents the surface free energy of the solid – liquid's surface tension, γ_L represents the surface free energy of the liquid's surface tension, and θ represents the contact angle.

Initial studies on wettability and contact angle measurements involved placing a drop of liquid onto the wood surface, generally measuring only the instantaneous or equilibrium contact angles (Herczeg 1965). However, due to the wood's porous structure and surface roughness, more accurate measurements to describe the wetting process were needed (Gray 1962). The dynamic contact angle measured by the Wilhelmy plate technique is more sensitive to predicting perimeter changes in the wood due to its accounting of the intricacies of the wood surface on a microscopic scale (Son and Gardner 2004). The downward force of a wood sample hanging perpendicular to the liquid's surface is measured. When the wood initially contacts the liquid, the equilibrated force can be expressed as

$$F = \gamma * P * \cos\theta \tag{4.2}$$

where F is the force on the object, γ is the surface tension of the liquid, P is the wetted perimeter, and θ is the contact angle between the solid and the liquid. When the sample is partially immersed in the liquid, a buoyancy correction is included in the equation. Thus,

$$F = \gamma * P * \cos\theta - (\rho * V) \tag{4.3}$$

where ρ is the density of the liquid and V is the volume of the solid.

A Thermo Cahn DCA 322 was used for the dynamic contact angle measurement. Four probe liquids, α-bromonapthalene, ethylene glycol, formamide, and water, with known surface tension components were used (Table 4.1) (Wu et al. 1995). About eighty milliliters of probe liquid were poured into a beaker and placed on a moving stage mechanism. The sample was clipped and hung perpendicular to the liquid's surface. It was then balanced to within ± 1 mg by adding a stirrup and counterweights (Figure 4.2). When the balance became stationary, the test was initiated. The stage was operated by a motor, rising at 264 microns – per – second. Force and depth data were collected to 4.0 mm upon sample and liquid contact at the zero depth of immersion. WinDCA software calculated the advancing dynamic contact angle.

Table 4.1

Surface tension and components (mJ/M^2) of the probe liquids.

Probe Liquid	γ_L	γ_L^d	γ_L^p
α-Bromonapthalene	44.4	44.4	0.0
Ethylene Glycol	48.0	29.0	19.0
Formamide	58.0	39.0	19.0
Water	72.8	21.8	51.0

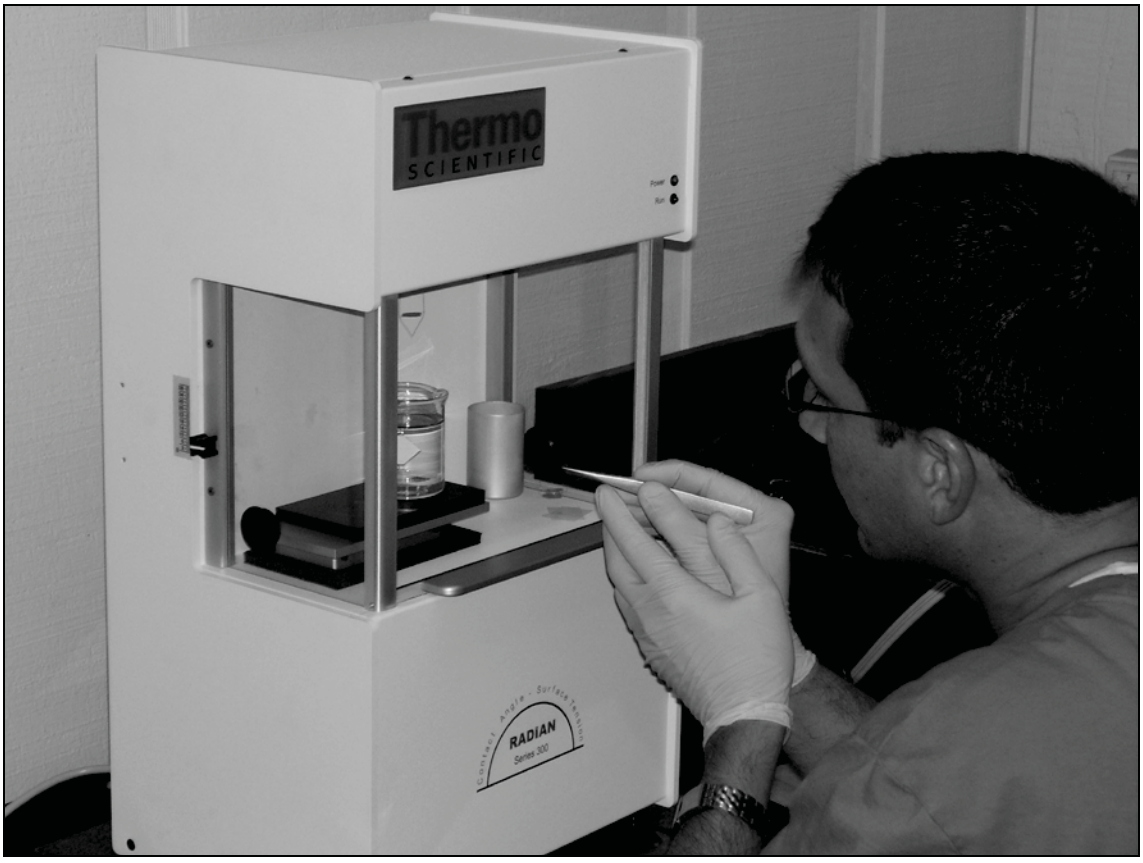

Figure 4.2

Counterbalancing the Thermo Cahn DCA 322.

A combination of Young's equation (1805), Good's and Girifalco's geometric mean law (1957), and Fowkes' equation (1962) describing the dispersive and polar components of surface energy was used to determine the surface energy of each wood/treatment combination

$$\frac{(1+\cos\theta)*\gamma_L}{2*(\gamma_L^d)^{0.5}} = (\gamma_S^d)^{0.5} + (\gamma_S^p)^{0.5} * \left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{0.5} \quad (4.4)$$

where θ represented the mean contact angle in the liquid, γ_L represented the surface tension of the liquid, γ_L^d and γ_S^d represented the surface free energy from London dispersion forces of the liquid and the wood, and γ_L^p and γ_S^p represented the surface free energy from the dipole-dipole interactions of the liquid and wood. The unknown parameters of each wood /treatment combination, γ_S^d and γ_S^p, were calculated using simultaneous equations for each probe liquid (Gardner 1996; Shi et al. 1997). The simultaneous equations were solved using simple linear regression in SAS 9.1.3 (2003). The model used for the analysis was

$$Y = \beta_0 + \beta_1 X + \varepsilon \quad (4.5)$$

where Y represented the dependent variable $\frac{(1+\cos\theta)\gamma_L}{2\left(\gamma_L^d\right)^{0.5}}$, x represented the independent variable $\left(\frac{\gamma_L^p}{\gamma_L^d}\right)^{0.5}$, β_0 represented the intercept $\left(\gamma_S^d\right)^{0.5}$, β_1 represented the slope $\left(\gamma_S^p\right)^{0.5}$, and ε represented the error of the model. The intercept and slope were squared to determine the dispersive and polar forces. The solid surface energy, γ_S, was then calculated by

$$\gamma_S = \left(\gamma_S^d\right) + \left(\gamma_S^p\right) \tag{4.6}$$

Results and Discussion

An example contact angle run is shown in Figure 4.3 (see Appendix A for advancing contact angle information). An increase in friability was generally observed on the treated wood samples compared to the controls. The presence of an acid or caustic in a treating solution accelerates wood degradation with acid being the more severe of the two. This degradation may have contributed to the variability in the acid treatments. The water treatment became a weak acid over time as acetyl groups are hydrolyzed, resulting in some autohydrolysis of hemicelluloses by the acetic acid.

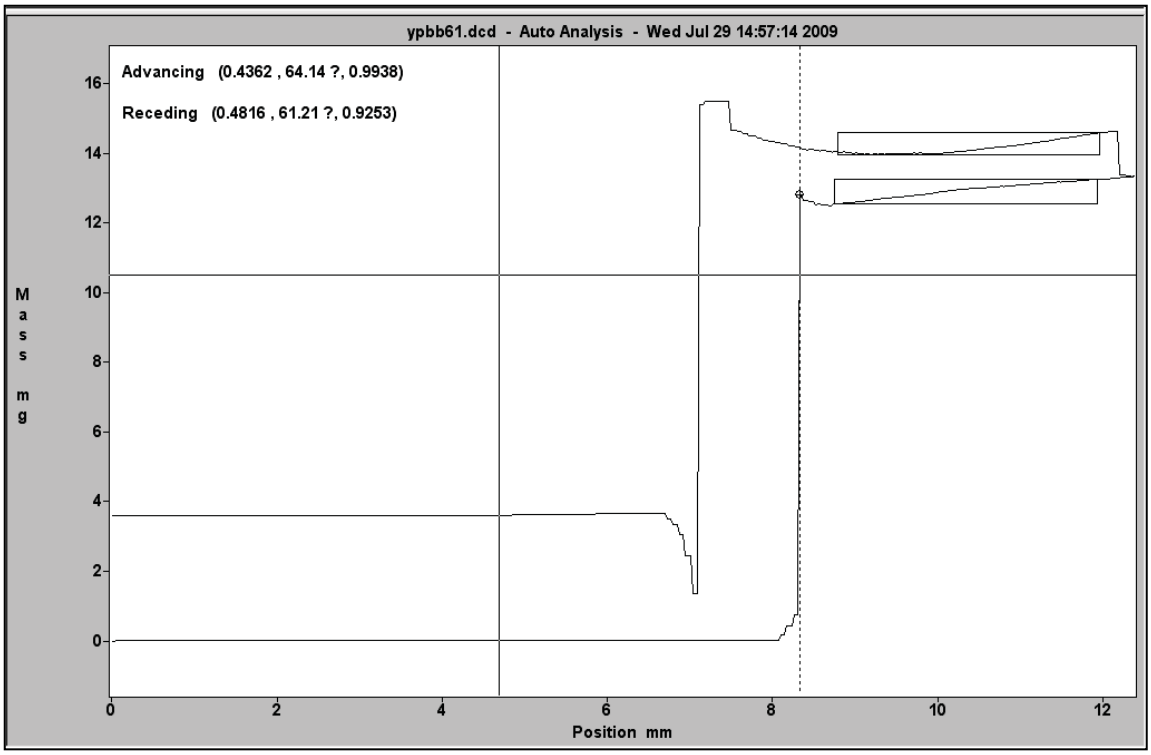

Figure 4.3

Dynamic contact angle run of Yellow-poplar/NaOH in α-bromonapthalene.

The calculated results of solid surface energy components, γ_S^d and γ_S^p, and the total surface energy, γ_S, are listed in Table 4.2 with the majority of the wood/treatment combinations surface energies being accounted for by the dispersive forces. The polar and dispersive forces significantly correlated with one another across the treatments (R^2 = 0.79, Figure 4.4). As the dispersive forces increased the polar forces decreased. The highest improvements on the dispersive component were obtained by the acid treatment. Caustic treatment generally did not improve the treated woods' dispersive components. The acid treatment notably reduced the polar component for each species, 8.1 mJ/M^2 for red oak, 15.4 mJ/M^2 for sweetgum, and 4.8 mJ/M^2 for yellow-poplar. The water and base

treatments increased the polar component for red oak, decreased it for yellow-poplar, with mixed results for sweetgum. The total surface energy for red oak consistently increased compared to the control. The total surface energy of sweetgum increased in acid, showed virtually no change in water, and decreased in a basic treatment. Yellow-poplar's total surface energy increased in both an acid and water treatment and decreased in a base solution. The acid and water treatments produced higher overall surface energies.

Table 4.2

Total surface energy (mJ/M^2) of the wood/treatment combinations and its components based on regression analysis of four probe liquids.

Treatment Combination	γ_S^d	γ_S^p	γ_S
Red Oak/H_2SO_4	46.4	3.4	49.7
Red Oak/Water	32.1	18.2	50.4
Red Oak/NaOH	27.6	19.4	47.0
Red Oak/Control	32.6	11.5	44.1
Sweetgum/H_2SO_4	51.9	2.7	54.7
Sweetgum/Water	31.3	18.3	49.6
Sweetgum/NaOH	29.0	16.6	45.6
Sweetgum/Control	31.0	18.1	49.1
Yellow-poplar/H_2SO_4	41.8	14.4	56.1
Yellow-poplar/Water	35.5	17.6	53.2
Yellow-poplar/NaOH	31.5	16.0	47.5
Yellow-poplar/Control	31.5	19.2	50.7

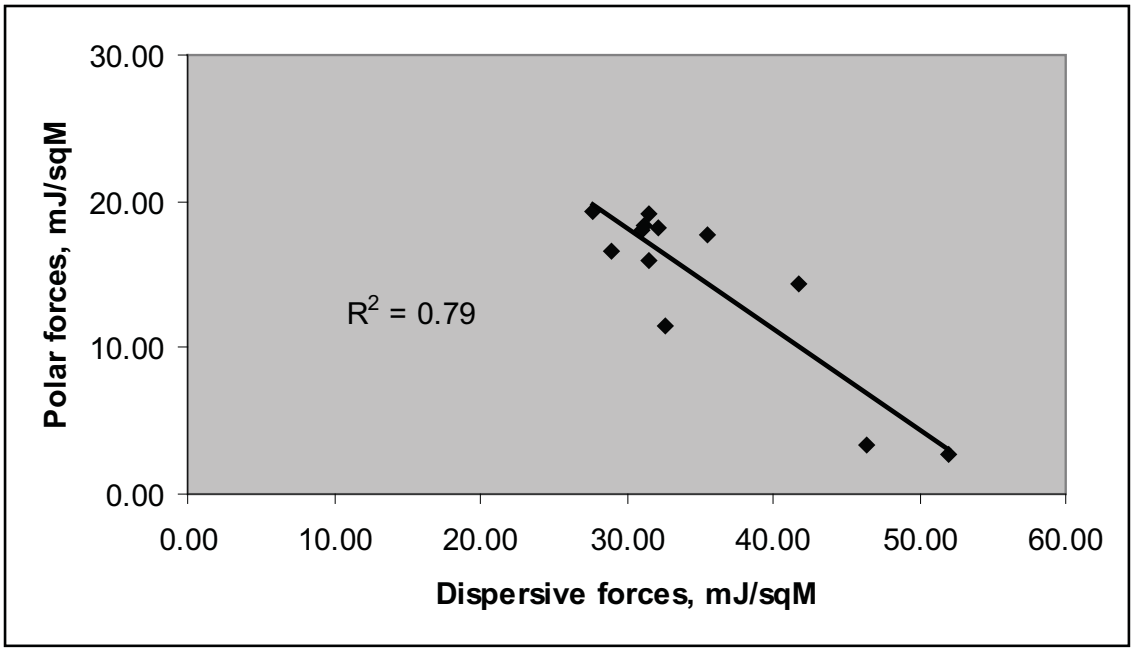

Figure 4.4

Plot of polar versus dispersive forces for the wood/treatment combinations.

Wood is heterogeneous in its chemical composition both between and within species. The pH of most woods is slightly acidic [red oak- 4.90, sweetgum- 5.30, yellow-poplar- 5.43] (Manwiller 1985). However, the surface chemistry reveals alkaline aromatic compounds are predominant in wood. Gardner (1996) concluded that the acid-base interaction component of the total surface energy of six hardwoods was dominated by the basic constituent due to the presence of aromatic compounds. The surface chemistry of the woods tended to exhibit an alkaline pH due to the predominance of electron donating sites contained within the wood extractives, even though the woods in the bulk form were slightly acidic. While red oak had a pH of 4.67 in bulk form, its surface was dominated by aromatics. The phenol content in red oak heartwood is high (Rowe and Connor 1979). Phenolic glycosides are abundant in sweetgum along with

cinnamic acid-containing storax. Yellow-poplar contains high amounts of alkaloids and sesqiterpenes. Shi et al. (1997) found similar results for wood fibers consisting of 75% aspen and 25% assorted hardwoods. De Meijer et al. (2000) concluded likewise for spruce and meranti.

The sulfuric acid treatments increased the wood surface energy by neutralizing the woods' surfaces. The water solutions generally become acidic as well as acetic acid is released during the autohydrolysis process, which in turn leads to further acetic acid formation (Connor 1984). Although sodium hydroxide hydrolysis initially increases wetting by swelling the wood cell wall (Stephen and Kutscha 1987), the effect of the sodium hydroxide treatment on the already alkaline surface worked to lower the surface energy for sweetgum and yellow-poplar due to the degradation of the cellular structure upon drying (Wangaard 1966). Red oak contains high amounts of acidic extractives, which contribute to poor adhesive bonding (Koch 1985). Sodium hydroxide had a neutralizing effect on those extractives, which would explain why an alkaline treatment increased the surface energy of red oak. The acid-treated yellow-poplar samples had a high degree of surface roughness, which contributed to an increased wetting performance (Stehr et al. 2001).

Conclusions

Contact angles of four probe liquids on three species treated in three solutions (1% sulfuric acid, water, and 1% sodium hydroxide) were compared with the untreated controls. The contact angles of yellow-poplar in acid were generally lower than that of the other treatments, likely due to the friability and surface roughness of the samples.

Acid-treated samples suffered some degradation, contributing to the variation within this treatment. Surface energy values were calculated for each wood/treatment combination and compared with the controls. The total surface energy of red oak was consistently increased by extraction in all treatments. The total surface energy of sweetgum was only improved by the acid treatment, while those of yellow-poplar were increased by both acid and water treatment solutions. Acid and water treatments likely increased the surface energy values by neutralizing the wood surface via extraction of soluble aromatic compounds. The alkaline treatment lowered the surface energy values of sweetgum and yellow-poplar. Dispersive forces were the large contributors to the woods' surface energies. Partially hydrolyzing these hardwoods in acid or water has the potential to improve wood adhesion for strand-based composites manufacturing.

Literature Cited

Beech JC (1975) The thickness swelling of particleboard. Holzforschung 29(1):11-18.

Bryant BS (1968) Studies in wood adhesion: interaction of wood surface and adhesive variables. Forest Prod J 18(6):157-162.

Carll CG (1996) Review of thickness swell in hardboard siding – Effect of processing variables. Gen Tech Rep FPL-GTR-96. USDA For Serv Forest Products Laboratory, Madison, WI. 10 pp.

Chen CM (1968) Effect of extractive removal on adhesion and wettability of some tropical woods. Forest Prod J 20(1):36-41.

Connor AH (1984) Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood Fiber Sci 16(2):268-277.

de Meijer M, Haemers S, Cobben W, Militz H (2000) Surface energy determinations of wood: comparison of methods and wood species. Langmuir 16:9352-9359.

Fernando S, Adhikari S, Chandrapal C, Murali N (2006) Biorefineries: Current status, challenges, and future direction. Energ Fuel 20:1727-1737.

Fowkes FM (1962) Determination of interfacial tensions, contact angles, and dispersion forces in surfaces by assuming additivity of intermolecular interactions in surfaces. J Phys Chem 66(2):382.

Gardner DJ (1996) Application of the Lifshitz-Van Der Waals acid-base approach to determine wood surface tension components. Wood Fiber Sci 28(4):422-428.

Gilbert N, Hobbs I., Sandberg W (1952) Utilization of wood by hydrolysis with dilute sulfuric acid. Forest Prod J 3:43-48.

Girafalco LA, Wood RJ (1957) A theory for the estimation of surface and interfacial energies. I. Derivation and application to interfacial tension. J Phys Chem 61:904.

Gray VR (1962) The wettability of wood. Forest Prod J 12(6):452-461.

Halligan AF (1970) A review of thickness swelling in particleboard. Wood Sci Technol 4(4):301-312.

Haupt RA, Sellers, Jr T (1994) Phenolic resin – wood interaction. Forest Prod J 44(2):69-73.

Herczeg A (1965) Wettability of wood. Forest Prod J 15(11):499-505.

Koch P (1985) *Utilization of Hardwoods Growing on Southern Pine Sites*. *Volume I: The Raw Material*. USDA For Serv Agricultural Handbook. 3710 p. US Government Printing Office, Washington DC.

Larmore FD (1959) Influence of specific gravity and resin content on properties of particleboard. Forest Prod J 9(4):131-134.

Manwiller FG (1981) Page 453 *in* P Koch *Utilization of Southern Hardwoods Growing on Southern Pine Sites*. USDA For Serv Agricultural Handbook, US Government Printing Office, Washington DC.

Nearn WT (1974) Application of ultrastructure concept in industrial wood products research. Wood Sci 6(3):285-293.

Paredes JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2009) Surface characterization of red maple strands after hot water extraction. Wood Fiber Sci 41(1):38-50.

Parham RA, Gray RL (1984) Formation and structure of wood. Pages 43-45 *in* RM Rowell *The Chemistry of Solid Wood*. American Chemical Society, Washington D.C.

Ragauskas AJ, Nagy M, Kim DH, Eckert CA, Hallett JP, Liotta CL (2006) From wood to fuels: Integrating biofuels and pulp production. Ind Biotechnol 2(1):55-65.

Rowe JW, Connor AH (1979) Extractives in eastern hardwoods. Gen Tech Rep FPL-GTR-18. USDA For Serv Forest Products Laboratory, Madison, WI. 72 pp.

SAS (2003) SAS Institute. Version 9.1.3. Cary, NC.

Schultz TP, Biermann C, McGinnis G (1983) Steam explosion of mixed hardwood chips as a biomass pretreatment. Ind Eng Chem Prod Res Dev 22(2):344-348

Shi Q, Gardner DJ, Wang JZ. (1997) Surface properties of polymeric automobile fluff particles characterized by inverse as chromatography and contact angle analysis. Pages 245-256 *in* International Conference of Woodfiber-Plastic Composites 4th Forest Products Society, Madison, WI.

Son J, Gardner DJ (2004) Dimensional stability measurements of thin wood veneers using the Wilhelmy plate technique. Wood Fiber Sci 36(1):98-106.

Stehr M, Gardner DJ, Walinder MEP (2001) Dynamic wettability of different machined wood surfaces. J Adhesion 76(3):185-200.

Stephen RS, Kutscha NP (1987) Effect of resin molecular weight on bonding flakeboard. Wood Fiber Sci 19(4):353-361.

Sun Y, Cheng J (2002) Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresource Technol 83:1-11.

Thomas RJ (1977) Wood: Structure and chemical composition. Pages 17-23 *in* IS Goldstein *Wood Technology: Chemical Aspects*. American Chemical Society, Washington D.C.

Wangaard F (1966) Resistance of wood to chemical degradation. Forest Prod J 16(2):53-64.

Wu W, Giese, Jr R, van Oss C (1995) Evaluation of the Lifshitz-van der Waal/acid-base approach to determine surface tension components. Langmuir 11(1):379-382.

Yoon HH (1998) Pretreatment of lignocellulosic biomass by autohydrolysis and aqueous ammonia percolation. Korean J Chem Eng 15(6):631-636.

Young T (1805) Phil. Trans. 95:65.

CHAPTER V

RESISTANCE OF MODIFIED HARDWOOD MATERIAL TO SUBTERRANEAN TERMITE ATTACK

Introduction

Biological durability is a growing issue in wood composites as the industry continues to gain market share and species utilization diversifies. Durability is a particular issue in the southern United States as termites alone inflict extensive economic losses. Hardwoods, such as yellow-poplar (*Liriodendron* tulipifera L.), sweetgum (*Liquidambar* styraciflua L.), and red oak (*Quercus* spp.), are currently used on a limited basis in wood composites even though they are present in high volumes across the South. One reason for that is soluble compounds in various hardwoods, such as oak, interfere with adhesion during resin blending and pressing (Beech 1975). However, some of these problems can be solved by chemical treatment. A hydrothermal treatment improved the wettability of red maple for oriented strand board (OSB) by removing extractives along with some hemicelluloses and lignin (Mills et al. 2009; Paredes et al. 2009). In addition, fungal durability of the composite was maintained or improved (Howell et al. 2009). The overall objective of this research is to improve the properties of three underutilized southern hardwoods for manufacturing structural composite lumber. The specific objective of this chapter was to understand how hydrolysis in pressurized, high

temperature conditions would affect the woods' susceptibility to termite degradation by the eastern subterranean termite (*Reticulitermes flavipes* Kollar).

Experimental

Design

Yellow-poplar, sweetgum, and red oak specimens machined from green lumber prior to this experiment measuring 3 mm x 15 mm x 150 mm (T x R x L) were retrieved from storage at 2°C then water saturated. Each sample was treated in a 2 L reactor (Parr 4843) at 150°C for 30 minutes with either water or 1.0% sodium hydroxide (NaOH). Untreated controls were also utilized. Five replications were performed over 5 days for blocking of each species/treatment combination (n=45). A randomized complete block design (RCB) was constructed using the model

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + \delta_k + e_{ijk} \quad (5.1)$$
$$\text{where } \delta_k \sim N(0, \sigma_\delta^2), \text{ iid}$$
$$e_{ijk} \sim N(0, \sigma^2), \text{ iid} \quad \text{Ind.}$$

where $\alpha_{i\ (i = 1, 2, ..., a)}$ represented the main effect due to Factor A [Species], $\beta_{j\ (j = 1, 2, ..., b)}$ represented the main effect due to Factor B [Solution], $(\alpha\beta)_{ij}$ represented the interaction of Factors A and B [Species x Solution], $\delta_{k\ (k = 1, 2, ..., r)}$ represented the block, and e_{ijk} represented the error of the model

The following hypotheses were tested:

- Block: Did the days vary relative to the response?
- Factor A: Did the species perform equally relative to the response?

- Factor B: Did the treating solutions perform equally relative to the response?
- Factor A x B: Was the response to the treating solution equal across the species?

Methods

After treatment, the samples were placed in a convection oven at a temperature of 103 ± 2°C to obtain oven-dry weight. They were then placed in a dehumidification kiln at 21 ± 2°C and 41 ± 5% relativity humidity (RH) until a constant weight was achieved at this equilibrium moisture content (EMC) environment. The volume was then calculated by measuring the beams' dimensions. Specific gravity (SG) of each specimen was determined by oven-dry weight divided by the EMC volume.

The guidelines for the no-choice test procedure described in AWPA Standard E1-09 were observed for this initial study (AWPA 2009). One 60 mm section was cut from each miniature beam. The initial weights were recorded, and samples were subsequently situated with 2 corners along one side in test jars (80 mm x 100 mm) with 150 g of sand and 25 mL of deionized water. Four hundred termites of the species of *R. flavipes* were placed along the other side per AWPA E1. The test jars were placed in a conditioning chamber at 26 ± 2°C and 55 ± 5% RH for 28 days for optimal termite feeding.

Following exposure, the samples were removed from the jars and brushed clean. They were dried at 21 ± 2°C and 41 ± 5% RH. The samples were reweighed and mass loss (%) was determined. Results were analyzed using analysis of variance (ANOVA)

and linear regression with a 0.05 level of significance. Multiple comparisons were made using Fisher's protected least significant difference in SAS 9.1.3 (2003).

Results and Discussion

Each factor independently and significantly affected the mean mass loss due to termite feeding (Table 5.1) with species being the more significant of the two [species, $p<0.0001$; treatment, $p=0.0004$]. Yellow-poplar averaged significantly more termite deterioration across the treatments than the other two species [yellow-poplar-84.6%, sweetgum-60.8%, red oak-51.7%]. Termites tend to show a preference to wood with a lower specific gravity, e.g. the earlywood of southern pine prior to the latewood as illustrated in the AWPA E1 standard (AWPA 2009). While the hydrolysis-treated samples were not statistically different, they did have significantly higher mean mass losses due to termite feeding than the controls [water-73%, NaOH-71%, control-53%].

Table 5.1

Average specific gravity at 21 ± 2°C and 41 ± 5% RH and mass loss, % (standard deviation), when exposed to *R. flavipes*.

Species	Treatment	Specific Gravity	% Mass Loss
Yellow-poplar	Water	0.37	95.1 (6.7)
	NaOH	0.43	91.0 (7.0)
	Control	0.38	67.5 (36.3)
Sweetgum	Water	0.62	64.6 (4.0)
	NaOH	0.65	62.7 (5.7)
	Control	0.61	55.2 (3.0)
Red Oak	Water	0.73	59.2 (6.4)
	NaOH	0.75	59.0 (5.3)
	Control	0.64	36.9 (6.0)

Hydrolyzing wood in water and NaOH solubilizes both nonstructural and structural components (Rowell 1984). Wood extractives particularly phenolics containing antioxidants possess termite toxicity and/or repellant properties (Little et al. 2010). Therefore, removing extractives via hydrolysis may lower wood's termite resistance. Another factor is treating in water at 150°C would release some of the acetyl groups, increasing the water acidity to result in some autohydrolysis of the cellulose to lower its degree of polymerization (DP) (Connor 1984). Further, heating cellulose in basic water solutions is known to lower the DP via peeling reactions and random scission (e.g. Sjöström 1993). It has been shown that decreasing cellulose DP resulted in greater termite degradation (Katsumata et al. 2007). Thus, the enhanced termite deterioration for the chemically-treated wood samples might be due to the reduction of cellulose DP.

It was generally observed using leftover portions of the samples that those subjected to the treatments became more friable when tested with a razor blade versus the controls. Hydrolysis with NaOH particularly degrades the structural components of wood (Wangaard 1966). It is therefore possible that this degradation to make the wood more friable also increased its susceptibility to subterranean termites. Behr et al. (1972) conducted tests using several southern hardwoods, including yellow-poplar, and found that *R. flavipes* feeding was inversely proportional to wood hardness. The same effect was observed in this study, where mass loss and specific gravity were significantly and negatively correlated for both the treated (water and NaOH) and untreated samples (Figure 5.1). As specific gravity increased (i.e. the species effect), mass loss decreased for the samples.

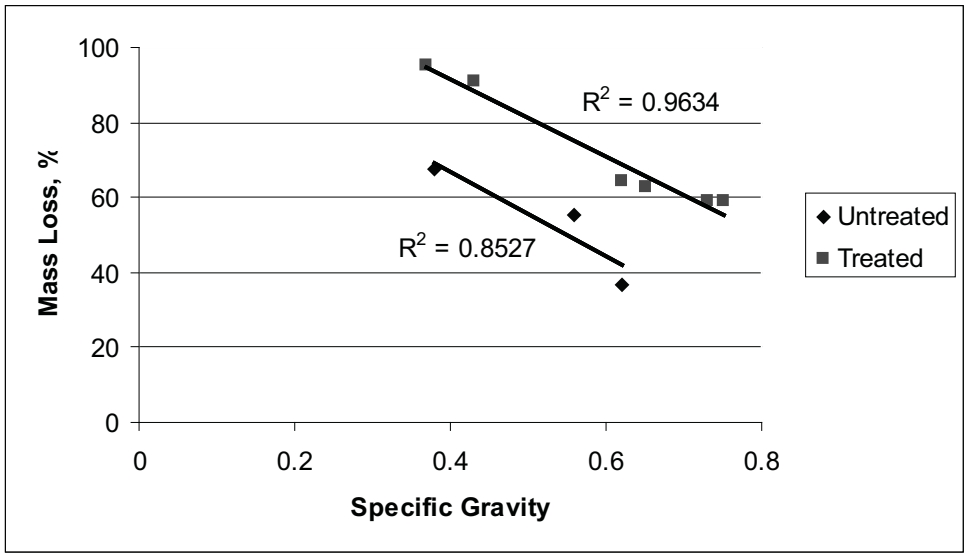

Figure 5.1

Plot of mass loss (%) versus specific gravity at 21 ± 2°C and 41% ± 5%RH for the treated and untreated means. R^2 for each regression line is also displayed. Treated samples include both water and NaOH as they were not significantly different at $\alpha = 0.05$.

Conclusions

Treating southern hardwoods at 150°C in water or 1.0% NaOH significantly increased their susceptibility to termite deterioration. This may, in part, be caused by the removal of soluble components along with the increased friability of the modified wood material. Termite feeding was also highly related to the wood specific gravity. The mass loss decreased as the specific gravity increased for both the treated (water and NaOH) and untreated samples. Employing a choice test of beams made from treated and untreated southern hardwood flakes at different target densities to compare with southern pine structural composite lumber may provide a better understanding of the roles that specific gravity and chemical treatment play on termite deterrence.

Literature Cited

AWPA (2009) Standard method for laboratory evaluation to determine resistance to subterranean termites. E-1-09. American Wood Protection Association, Birmingham, AL.

Beech JC (1975) The thickness swelling of particleboard. Holzforschung 29(1):11-18.

Behr EA, Behr CT, Wilson LF (1972) Influence of wood hardness on feeding by the eastern subterranean termite, Reticulitermes flavipes (Isoptera: Rhinotermitadae). Ann Entomol Soc Am 65(2):467-460.

Connor AH (1984) Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood Fiber Sci 16(2):268-277.

Howell C, Paredes JJ, Jellison J (2009) Decay resistance properties of hot water extracted oriented strandboard. Wood Fiber Sci 41(2):201-208.

Katsumata N, Yoshimura T, Tsunoda K, Imamura Y (2007) Resistance of gamma-irradiated sapwood of *Cryptomeria japonica* to biological attacks. Wood Sci 53:320-323.

Little NS, Schultz TP, Nicholas DD (2010) Termite-resistant heartwood: Effect of antioxidants on termite feeding deterrence and mortality. Holzforschung 64(3)395-398.

Mills RH, Jara J, Gardner DJ, van Heiningen A (2009) Inverse gas chromatography for determining the surface free energy and acid-base chemical charactristics of a water extracted hardwood (*Acer rubrum*). J Wood Chem 29:11-23.

Paredes JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2009) Surface characterization of red maple strands after hot water extraction. Wood Fiber Sci 41(1):38-50.

Rowell RM (1984) Penetration and reactivity of cell wall components. Pages 77-78 *in* RM Rowell, ed., The chemistry of solid wood. American Chemical Society, Washington DC.

SAS (2003) SAS Institute. Version 9.1.3. Cary, NC.

Sjöström E (1993) Wood chemistry: Fundamentals and applications. Academic Press, San Diego, CA. 293 pp.

Wangaard FF (1966) Resistance of wood to chemical degradation. Forest Prod J 16(2):53-64.

CHAPTER VI

EVALUATION OF HOLOCELLULOSE CONTENT OF PARTIALLY HYDROLYZED HARDWOODS AND ITS EFFECT ON WOOD PROPERTIES

Introduction

Conversion of lignocellulosic materials, including wood, to ethanol has become a primary agricultural policy concern. Small stems from low-value hardwood species provide an excellent feedstock source for the biorefinery. These stems are primarily early- to mid-successional species, such as red oak (*Quercus* spp.), sweetgum (*Liquidambar* styraciflua L.), and yellow-poplar (*Liriodendron* tulipifera L.), among others, that compete with southern pine on many sites. Rather than adding cost to their timber investment by applying expensive silvicultural treatments, landowners can have these stems harvested for biofuel conversion.

However, the refining process completely hydrolyzes the lignocellulosic material to maximize sugar yield by using a combination of extreme temperatures and harsh chemicals. A byproduct consisting of mainly lignin, for which there is little value, is primarily burned for energy onsite. High input costs coupled with low output revenues due to a lack of added value being realized from the conversion process currently leaves lignocellulosic ethanol cost prohibitive. Therefore, an alternative lignocellulosic conversion process needs to be investigated in order to give added 1) wealth to the

landowner, 2) productivity to the logger, and 3) revenue streams to the production facility.

One option would employ relatively low temperatures and chemical concentrations, which would only partially hydrolyze the wood. This would result in forming some hydrolyzed sugars to ferment for conversion to ethanol while leaving behind a modified wood byproduct that remains structurally whole rather than being pulped to individual fibers. This byproduct could add value to the conversion process as a wood composites raw material, with possibly improved properties. However, few studies have been conducted on wood properties following treatment in a heated solution (Ragauskas et al. 2006; Hill 2006).

Wood heated in solution under pressurized conditions undergoes many mechanical, physical, and chemical modifications due to changes in the chemistry of the wood cell wall brought about by hydrolysis. The extractives are the first constituents removed as they are nonstructural components and of low molecular weight (Parham and Gray 1984). Carbohydrates, particularly the hemicelluloses, are also susceptible to chemical reactions and are isolated rather easily from the wood cell wall (Rowell et al. 1988).

Temperature is a key component in the hydrolysis process as high temperatures solubilize acidic components in the hemicelluloses of wood (Li et al. 2010). Heating wood in water results in autohydrolysis by which acetic acid is released by hydrolysis of hemicellulose acetate by water (Connor 1984). Krhol and Gromov (1976) demonstrated that autohydrolysis at temperatures ranging from 100^{o}C to 180^{o}C altered the chemical composition of wood. The intensity of the transformations increased with the rise in

temperature. A rapid first stage was noted as easily hydrolyzed substances, mostly pentosans, were removed by formation of organic acids causing a reduction of the solution's pH value. A second stage was noted as isolation of other components continues but at a much slower rate. Little cellulose is extracted below 230°C (Garrote et al. 1999). Further, heating wood in alkaline solutions is known to catalyze the hydrolysis process as well as lower cellulose degree of polymerization (DP) through peeling reactions and random scission (Sjöström 1993) while treating wood in acid quickens the decrease in cellulose DP (Winandy and Lebow 2001). Extraction rates tend to be curvilinear, leveling with time (Harris et al. 1958; Khrol and Gromov 1976).

These changes generally result in lower mechanical properties (Thompson 1969), significant weight losses (Paredes et al. 2008), increased dimensional stability (Rowell 1988), and decreased biodegradation due to decay fungi (Howell et al. 2009). Most extractives and hemicelluloses are removed (Mills et al. 2009) as wettability increases (Paredes et al. 2009). Studies in this dissertation found likewise for specific modulus and mass loss and wettability, but biodegradation due to termite feeding was actually found to increase (McConnell et al. 2010).

The purpose of this study was to study the effect of a partial hydrolysis on the polysaccharide composition of modified red oak, sweetgum, and yellow-poplar wood. The holocellulose content of the treated woods was then compared with untreated controls. The changes in holocellulose were then used to predict the accompanying changes in specific modulus, mass loss due to treatment, surface free energy, and termite resistance that have been previously reported.

Experimental

Materials

Yellow-poplar, sweetgum, and red oak specimens machined from green lumber measuring 3 mm x 15 mm x 150 mm (T x R x L) were retrieved from storage at 2°C then water saturated. Each sample was treated in a 2 L reactor (Parr 4843) at 150°C for 30 minutes with 1.0% sulfuric acid (H_2SO_4), water or 1.0% sodium hydroxide (NaOH). Untreated hardwood controls were also utilized. Six replicates per treatment combination were performed.

Methods

The samples were conditioned in a chamber at 21 ± 2°C and 41 ± 5% relative humidity to a constant weight. The six replicates for each wood/treatment combination were ground in a Wiley mill to a size 20 mesh. Extractive-free wood was prepared following the guidelines of ASTM D 1105-96 with the exception of extracting reagents, which were a 1:1 mixture of methanol and benzene [600 mL total] (ASTM 1996). A Soxhlet apparatus was used for the reaction, which was allowed to run for 6 hours. The meal was placed in a petri dish and left to dry for 24 hours, and then placed in a sealed plastic bag to equilibrate. The wood meal was analyzed gravimetrically on a wet chemistry basis for extracted contents and moisture content (total solids). Total solids content was determined after oven-drying for 5 hours at 104 ± 5°C.

Holocellulose was measured gravimetrically on extractives-free wood on a wet basis following ASTM D1104-56 (ASTM 1956). One hundred fifty milliliters of distilled water was added to 2.5 grams of wood powder. The beaker was heated in a

water bath to 75°C. Each hour for 5 hours 10 drops of glacial acetic acid and 1.5 grams of sodium chlorite were added, and the beaker was vigorously stirred. After 5 hours, the solution was filtered through a coarse sintered glass filter using an aspirator. The filtrate was washed with distilled water to neutrality followed by acetone. The filtrate was left to dry overnight. Holocellulose content was determined after oven-drying for 5 hours at 104 ± 5°C. Two replicates were performed. Results were analyzed using analysis of variance (ANOVA) with an alpha = 0.05 level of significance. Multiple comparisons were made using Fisher's protected least significant difference. Simple linear regression was used to determine the holocellulose content's ability to explain the changes in specific modulus, mass loss due to treatment, surface free energy, and mass loss due to termite feeding by calculating the coefficient of determination (R^2). SAS 9.1.3 (2003) was used for all analyses.

Design

A completely randomized (CR) design was constructed.

This CR design utilized the model

$$Y_{ijk} = \mu + \alpha_i + \beta_j + (\alpha\beta)_{ij} + e_{ijk} \quad (6.1)$$
$$\text{where } e_{ijk} \sim N(0, \sigma^2), \text{ iid}$$

where $\alpha_{i\ (i = 1, 2, ..., a)}$ represented the main effect due to Factor A [Species], $\beta_{j\ (j = 1, 2, ..., b)}$ represented the main effect due to Factor B [Solution], $(\alpha\beta)_{ij}$ represented the interaction of Factors A and B [Species x Solution], and e_{ijk} represented the error of the model.

The following hypotheses were tested.

- Factor A: Did the species perform equally relative to the response?

- Factor B: Did the treating solutions perform equally relative to the response?
- Factor A x B: Was the response due to the solution equal across the species?

Simple linear regression used the model

$$Y = \beta_0 + \beta_1 X + \varepsilon \tag{6.2}$$

where Y represented the dependent response variable, x represented the independent variable, holocellulose content, β_0 represented the intercept, β_1 represented the slope, and ε represented the error of the model. R^2 was determined by using the sum of squares (SS) as

$$R_{yx}^2 = \frac{SS(Total) - SS(Error)}{SS(Total)} \tag{6.3}$$

Results

Analysis of Variance

Summary statistics for the holocellulose content of extractives-free wood are provided in Table 6.1. An overall holocellulose reduction of 11.0% was obtained by conducting a partial hydrolysis treatment. Extracted contents in each species controls represented the natural extractives content analyzed, 4.17% for red oak, 2.56% for sweetgum, and 2.49% for yellow-poplar respectively.

Table 6.1

Average holocellulose content (coefficient of variation) and reduction of the holocellulose fraction following treatment.

Species	Treatment	Holocellulose, %	Reduction, % of control
Red Oak	H_2SO_4	70.1 (0.10)	13.7
	Water	78.4 (0.09)	3.6
	NaOH	74.6 (0.00)	8.9
	Control	81.2 (0.52)	
Sweetgum	H_2SO_4	63.6 (0.44)	18.6
	Water	71.3 (0.00)	9.6
	NaOH	67.3 (0.74)	16.2
	Control	78.2 (0.63)	
Yellow-poplar	H_2SO_4	74.4 (0.11)	10.0
	Water	76.3 (0.75)	7.7
	NaOH	73.7 (0.54)	10.9
	Control	82.7 (0.12)	

Holocellulose content was significantly affected by the interaction between the wood species and the treating solutions ($p < 0.0001$). In each treatment holocellulose content was significantly lower in sweetgum than in red oak or yellow-poplar. Although sweetgum had the lowest carbohydrate content in untreated wood, sweetgum did retain less holocellulose following treatment than red oak and yellow-poplar. For each species, all treatments significantly lowered the holocellulose content as compared to the controls. An acid treatment produced carbohydrate reductions of at least 10%. An acid treatment also produced the lowest values in red oak and sweetgum while an alkaline treatment produced the lowest value in yellow-poplar (Table 6.2).

Table 6.2

Least significant difference (LSD) results for the holocellulose content treatment means. Means with the same capital letter were not significantly different at $\alpha = 0.05$. LSD = 0.71%.

Treatment	Holocellulose content, %	t Grouping
Yellow-poplar/Control	82.7	A
Red Oak/Control	81.2	B
Red Oak/Water	78.4	C
Sweetgum/Control	78.2	C
Yellow-poplar/Water	76.3	D
Red Oak/NaOH	74.6	E
Yellow-poplar/H_2SO_4	74.4	E
Yellow-poplar/NaOH	73.7	F
Sweetgum/Water	71.3	G
Red Oak/H_2SO_4	70.1	H
Sweetgum/NaOH	67.3	I
Sweetgum/H_2SO_4	63.6	J

Regressions

Overall

Of the properties analyzed in previous chapters, holocellulose content overall was able to explain a majority of the variation in specific modulus and mass loss due to treatment as R^2 for mass loss was 0.61 and specific modulus was 0.52 respectively (Figure 6.1 and Figure 6.2). The regressions for both treatment mass loss and specific modulus were also significant. Total carbohydrates did not accurately explain surface free energy ($R^2 = 0.04$) nor the woods' resistance to termite feeding ($R^2 = 0.07$). As a caveat, it should be noted that an $R^2 > 0.50$ was considered to be able to describe a response as a majority of the variation is accounted for in the independent variable.

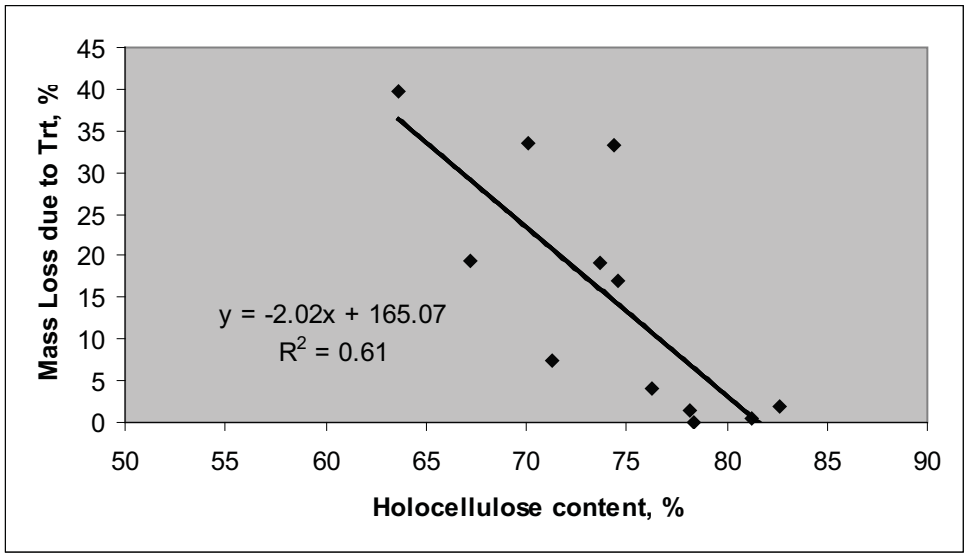

Figure 6.1

Regression model for explaining the mass loss due to treatment based upon holocellulose content following treatment.

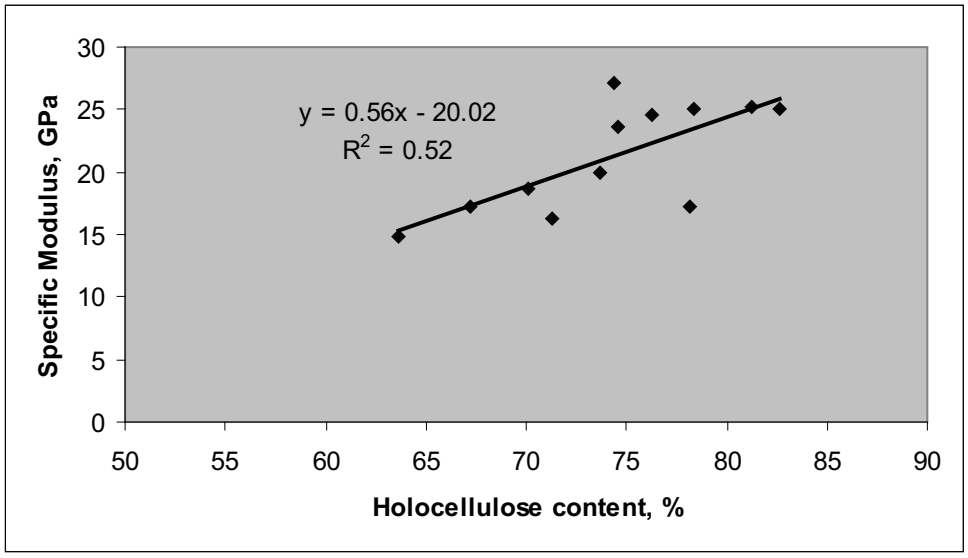

Figure 6.2

Regression model for explaining specific modulus based upon holocellulose content following treatment.

Species

The average response variables, surface energy (SE), mass loss due to treatment (ML), specific modulus (SM), and termite resistance (TR), from previous chapters and holocellulose content of treated and untreated wood from red oak, sweetgum, and yellow-poplar are given in Table 6.3 through Table 6.5. Coefficients of determination, R^2, illustrate that mass loss due to treatment and termite resistance were significantly explained in all three species by holocellulose content. Please note that termite resistance was not measured on acid-treated samples.

Red Oak

Generally speaking, partially hydrolyzing red oak resulted in an increased surface free energy, a significant mass loss, and a decrease in specific modulus. Termite resistance was significantly reduced. Holocellulose content was able to accurately explain the changes in mass loss due to treatment, specific modulus, and termite resistance but was unable to describe the changes in surface free energy.

Table 6.3

Regression model coefficients of determination, R^2, for each measured property based upon holocellulose content of red oak following treatment. **Bold** type denotes an accurate explanation.

Treatment	Holocellulose content, %	SE	ML	SM	TR
H_2SO_4	70.05	49.74	33.59	18.69	XX
Water	78.35	50.35	-0.02	25.05	59.19
NaOH	74.6	46.97	16.98	23.57	59.03
Control	81.2	44.11	0.43	25.27	36.87
R^2		0.32	**0.94**	**0.87**	**0.67**

Sweetgum

Partial hydrolysis of sweetgum resulted in a significant mass loss. However, there was no clear trend in regard to the effect on surface free energy and specific modulus. Treating sweetgum significantly lowered its termite resistance. Holocellulose content analysis was able to accurately explain the changes in mass loss due to treatment and termite resistance but was unable to describe the changes in surface free energy and specific modulus.

Table 6.4

Regression model coefficients of determination, R2, for each measured property based upon holocellulose content of sweetgum following treatment. **Bold** type denotes an accurate explanation.

Treatment	Holocellulose content, %	SE	ML	SM	TR
H_2SO_4	63.6	54.65	39.69	14.77	XX
Water	71.3	49.6	7.45	16.34	64.58
NaOH	67.25	45.59	19.39	17.3	62.69
Control	78.15	49.1	1.47	17.18	55.18
R^2		0.13	**0.85**	0.43	**0.71**

Yellow-poplar

Partial hydrolysis of yellow-poplar resulted in a significant mass loss, and decreased termite resistance. No clear trend was found in terms of the effect on the surface free energy and specific modulus. Holocellulose content was able to accurately explain the changes in mass loss due to treatment and termite resistance but was unable to describe the changes in surface free energy and specific modulus.

Table 6.5

Regression model coefficients of determination, R^2, for each measured property based upon holocellulose content of yellow-poplar following treatment. **Bold** type denotes an accurate explanation.

Treatment	Holocellulose content, %	SE	ML	SM	TR
H_2SO_4	74.41	56.14	33.31	27.15	XX
Water	76.26	53.17	4.13	24.61	95.14
NaOH	73.66	47.53	19.05	20.02	91.05
Control	82.66	50.68	1.80	25.12	67.48
R^2		0.01	**0.51**	0.09	**0.83**

Treatments

The average response variables from previous chapters and holocellulose content of red oak, sweetgum, and yellow-poplar are given for each treating solution in Table 6.6 through Table 6.8. Coefficients of determination, R^2, illustrate that specific modulus was accurately defined in all three treatments by holocellulose content.

Acid

Treating southern hardwoods in an acid solution consistently increased the surface free energy and resulted in a significant mass loss. No clear trend was found for the specific modulus. Holocellulose content was able to accurately explain the changes in mass loss due to treatment and specific modulus but was unable to describe the changes in surface free energy.

Table 6.6

Regression model coefficients of determination, R^2, for each measured property based upon holocellulose content of southern hardwoods following an acid treatment. **Bold** type denotes an accurate explanation.

Species	Holocellulose content, %	SE	ML	SM
Red Oak	70.05	49.74	33.59	18.69
Sweetgum	63.60	54.65	39.69	14.77
Yellow-poplar	74.41	56.14	33.31	27.15
R^2		0.01	**0.87**	**0.90**

Water

Treating southern hardwoods in water increased the surface free energy, decreased the specific modulus while the termite resistance was decreased for all three species. There was no clear trend for the mass loss affected by the treatment. Holocellulose content was able to accurately explain the changes in mass loss due to treatment and specific modulus when southern hardwoods were treated in water but was unable to describe the changes in surface free energy and termite resistance.

Table 6.7

Regression model coefficients of determination, R^2, for each measured property based upon holocellulose content of southern hardwoods following a water treatment. **Bold** type denotes an accurate explanation.

Species	Holocellulose content, %	SE	ML	SM	TR
Red Oak	78.35	50.35	-0.02	25.05	59.19
Sweetgum	71.3	49.6	7.45	16.34	64.58
Yellow-poplar	76.26	53.17	4.13	24.61	95.14
R^2		0.17	**0.92**	**0.94**	0.01

Base

Treating southern hardwoods in an alkaline solution resulted in significant mass losses due to both the treatments and termite feeding. Surface free energy and specific modulus results did not show a clear trend. Holocellulose content was able to accurately predict surface free energy and specific modulus.

Table 6.8

Regression model coefficients of determination, R^2, for each measured property based upon holocellulose content of southern hardwoods following an alkaline treatment. **Bold** type denotes an accurate explanation.

Species	Holocellulose content, %	SE	ML	SM	TR
Red Oak	74.6	46.97	16.98	23.57	59.03
Sweetgum	67.25	45.59	19.39	17.3	62.69
Yellow-poplar	73.66	47.53	19.05	20.02	91.05
R^2		**0.85**	0.49	**0.79**	0.09

Discussion

Overall, regression analyses revealed that a majority of the variation in mass loss caused by the treatments and specific modulus can be accounted for by the changes in total carbohydrate content following a partial hydrolysis of these hardwood species. The regressions for those two responses were significant. A distinct relationship was found for all three species between the holocellulose content of the wood following treatment and its subsequent mass loss as well as its termite resistance. A pattern was discerned for termite resistance as the regression model better explained termite degradation as activity increased. Yellow-poplar had both the lowest termite resistance and the highest coefficient of determination, followed by sweetgum and red oak. No specific trend was

found for mass loss as a function of the treatments. Each treatment was able to successfully explain the specific modulus based upon the holocellulose content. Water was the better descriptor among the three.

Treating wood in a heated environment alters the chemical structure of the wood cell wall, in turn changing the ultrastructure of the wood material due to the degradation of structural components (Baechler 1953; Biermann et al. 1984; Mills et al. 2009; Repellin and Guyonnet 2005). The extraction of soluble components further affects the wood's ability to retain its original identity, as changes in color, mass, volume, and tenacity, among others, take place (Hill 2006; McConnell et al. 2009; Wangaard 1966). Modifying the mass and volume subsequently alters the density of the treated wood, perhaps the most important predictor for mechanical properties of both solid wood and composite panels (Kellog and Ifju 1962; Blankenhorn et al. 1989). Changes in toughness of solid wood, for instance, were highly significant upon the changes in holocellulose content (Davis and Thompson 1964). Modulus of rupture (MOR) and work-to-maximum load are also dependent upon the holocellulose fraction (Wangaard 1966).

However, the results from this research suggest that there is no "silver bullet" explanation for these southern hardwood species' responses to a partial hydrolysis in the three solutions tested. The species examined have naturally different holocellulose contents and carbohydrate fractions. While the regressions for mass loss due to treatment and specific modulus were significant, neither showed a particularly strong relationship. This suggests other factors are at work.

Wangaard (1966) suggested that lignin content played a significant role in strength retention for wood subjected to an acid treatment. Hergert et al. (1977) showed

yellow-poplar having a lignin content of 30.3%; sweetgum and red oak contained 24.7% and 23.3% lignin respectively. While specific modulus values for red oak and sweetgum in the acid solution were statistically similar, they were significantly lower than the yellow-poplar/acid combination.

Looking closer at mass loss due to treatment and specific modulus, sweetgum overall appeared to be the most sensitive species. Pentosan content and wood degradation are directly related (Kass et al. 1970). Petterson (1984) and Hergert et al. (1977) stated that the pentosan hemicellulose content of sweetgum is higher than either red oak or yellow-poplar. Also, hemicelluloses are less resistant to hydrolysis than other structural components (Thompson 1969). The presence of an acid or alkaline catalyst can hasten the degradation of the hemicellulose fraction (Hill 2006).

Practically no relationship existed between holocellulose content and surface free energy or termite resistance as coefficients of determination were near zero. This may be due, in part, to the natural characteristics of the woods. One reason may be that the anatomical structure of the species may play a role in addition to the chemical makeup of the woods. For example, red oak is ring-porous while yellow-poplar and sweetgum are diffuse-porous hardwoods, but sweetgum's pores are very small compared with yellow-poplar's (Panshin and de Zeeuw 1980). This likely had an effect on the penetration of the treating solutions. Second, the extractives content in the controls (i.e. natural wood) were excellent predictors of surface free energy ($R^2 = 0.96$) and termite resistance ($R^2 = 0.87$). Gardner (1996) concluded extractives content was a primary indicator of surface free energy while Little et al. (2010) found that heartwood extractives containing antioxidants were effective at controlling termite activity.

The partial hydrolysis treatments left the woods brash and friable. Surface roughness in particular can affect the contact angle as the dynamic contact angle measured by the Wilhelmy plate technique can account for microscopic changes across the wood surface (Son and Gardner 2004; Stehr et al. 2001). Of the three treatments, the acid-treated woods were the most difficult to plane to a smooth surface. The friability may have been caused by the extraction of the hemicelluloses in association with the lowering of the cellulose degree of polymerization. Decreasing the cellulose polymer's chain length increases wood's susceptibility to termite attack (Katsumata et al. 2007). Additionally, wood hardness negatively correlates with termite resistance (Behr et al. 1972).

Conclusions

The polysaccharide contents of red oak, sweetgum, and yellow-poplar partially hydrolyzed in three solutions at 150°C for 30 minutes were determined. The greatest reduction in holocellulose content was obtained in an acid treatment, followed by the alkaline solution and water respectively. Sweetgum was the most susceptible to holocellulose extraction, likely due to its high pentosan content within the holocellulose fraction. Overall, a majority of the variation in mass loss caused by the treatment and the specific modulus was accounted for by changes in holocellulose content following the partial hydrolysis. The carbohydrate fraction was a good predictor of mass loss due to treatment and termite resistance for all three species while specific modulus was accurately predicted for all treating solutions.

Literature Cited

ASTM (1956) D 1104-56. Standard test method for holocellulose in wood. American Society for Testing and Materials, West Conshohocken, PA.

ASTM (1996) D 1105-96. Standard test method for preparation of extractive-free wood. American Society for Testing and Materials, West Conshohocken, PA.

Baechler RH (1954) Wood in chemical engineering construction. Forest Prod J 4(5):332-336.

Behr EA, Behr CT, Wilson LF (1972) Influence of wood hardness on feeding by the eastern subterranean termite, Reticulitermes flavipes (Isoptera: Rhinotermitadae). Ann Entomol Soc Am 65(2):467-460.

Biermann CJ, Schultz TP, McGinnis GD (1984) Rapid steam hydrolysis/extraction of mixed hardwoods as a biomass pretreatment. J Wood Chem Technol 41(1):111-128.

Blankenhorn PR, Labosky, Jr P, Stover LR, Nicholls D (1989) Selected chemical modifications of red oak and hard maple flakes for flakeboard manufacturing. Wood Fiber Sci 21(2):169-176.

Connor, A (1984) Kinetic modeling of hardwood prehydrolysis. Part I. Xylan removal by water prehydrolysis. Wood Fiber Sci 16(2):268-277.

Davis, WH, Thompson WS (1964) Influence or thermal treatments of short duration on the toughness and chemical composition of wood. Forest Prod J 14(8):350-356.

Gardner DJ (1996) Application of the Lifshitz-Van Der Waals acid-base approach to determine wood surface tension components. Wood Fiber Sci 28(4):422-428.

Garrote G, Dominguez H, Parajo JC (1999) Hydrothermal processing of lignocellulosic materials. Holz Roh Werkst 57(1999):191-202.

Harris JF, Saeman JF, Locke EG (1958) Chemical conversion of wood residues Part I: Separation and utilization of hardwood hemicelluloses. Forest Prod J 8(9):248-252.

Hergert, H, Sloan T, Gray J, Sandberg K (1977) The chemical composition of southeast hardwoods. *In* Peter Koch Utilization of Southern Hardwoods Growing on Southern Pine Sites. United States Department of Agriculture Forest Service Agriculture Handbook, United States Government Printing Office, Washington D.C. p. 368.

Hill C (2006) Wood Modification. Chemical, Thermal and Other Processes. Wiley & Sons, Sussex, England. 239 pp.

Howell C, Paredes JJ, Jellison J (2009) Decay resistance properties of hot water extracted oriented strandboard. Wood Fiber Sci 41(2):201-208.

Kass, A, Wangaard F, Schroeder H (1970) Chemical degradation of wood: The relationship between strength retention and pentosan content. Wood Fiber Sci. 2(1):31-39.

Katsumata N, Yoshimura T, Tsunoda K, Imamura Y (2007) Resistance of gamma-irradiated sapwood of *Cryptomeria japonica* to biological attacks. Wood Sci 53:320-323.

Kellog RM, Ifju G (1962) Influence of specific gravity and certain other factors on the tensile properties of wood. Forest Prod J 12(10):463-470.

Khrol YS, Gromov VS (1976) Chemical changes in hardwood during hydrothermal treatment. *In* TA Darzinsh Modification of Wood. United States Department of Agriculture Forest Service and National Science Foundation, Washington D.C. pp. 57-76.

Li H, Saeed A, Jahan MS, Ni Y, van Heiningen A (2010) Hemicellulose removal of hardwood chips in the pre-hydrolysis step of the kraft-based dissolving pulpproduction process. J Wood Chem Technol 30(1):48-60.

Little NS, Schultz TP, Nicholas DD (2010) Termite-resistant heartwood: Effect of antioxidants on termite feeding deterrence and mortality. Holzforschung 64(3):395-398.

McConnell TE, Shi SQ, Shmulsky R (2009) A preliminary study on the bending stiffness of chemically treated wood material for structural composite lumber. Wood Fiber Sci 41(3):322-324.

McConnell, TE, Little NS, Shi SQ, Schultz TP. 2010. The susceptibility of chemically treated southern hardwoods to subterranean termite attack. Wood Fiber Sci 42(2):252-254.

Mills RH, Jara J, Gardner DJ, van Heiningen A (2009) Inverse gas chromatography for determining the surface free energy and acid-base chemical charactristics of a water extracted hardwood (*Acer rubrum*). J Wood Chem 29:11-23.

Panshin A, de Zeeuw C (1980) Textbook of Wood Technology: Structure, Identification, Properties, and Uses of the Commercial Woods of the United States and Canada. Fourth Edition. McGraw-Hill, Inc., New York. 722 pp.

Paredes, JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2008) Influence of hot water extraction on the physical and mechanical behavior of OSB. Forest Prod. J. 58(12):56-62.

Paredes JJ, Mills R, Shaler SM, Gardner DJ, van Heiningen A (2009) Surface characterization of red maple strands after hot water extraction. Wood Fiber Sci 41(1):38-50.

Parham RA, Gray RL (1984) Formation and structure of wood. Pages 43-45 *in* RM Rowell *The Chemistry of Solid Wood.* American Chemical Society, Washington D.C.

Petterson RC (1984) The chemical composition of wood. Pages 57-126 *in* RM Rowell *The Chemistry of Solid Wood.* American Chemical Society, Washington D.C.

Ragauskas AJ, Nagy M, Kim DH, Eckert CA, Hallett JP, Liotta CL (2006) From wood to fuels: Integrating biofuels and pulp production. Ind Biotechnol 2(1):55-65.

Repellin V, Guyonnet R (2005) Evaluation of heat treated wood swelling by differential scanning calorimetry in relation to chemical composition. Holzforschung 59(1):28-34.

Rowell RM, Youngquist JA, Montrey HM (1988) Chemical modification: Adding value through new FPL composite processing technology. Forest Prod J 38(7/8):67-70.

SAS (2003) SAS Institute. Version 9.1.3. Cary, NC.

Sjöström E (1993) Wood Chemistry: Fundamentals and applications. Academic Press, San Diego, CA. 293 pp.

Son J, Gardner DJ (2004) Dimensional stability measurements of thin wood veneers using the Wilhelmy plate technique. Wood Fiber Sci 36(1):98-106.

Stehr M, Gardner DJ, Walinder MEP (2001) Dynamic wettability of different machined wood surfaces. J Adhesion 76(3):185-200.

Thompson WS (1969) Effect of steaming and kiln drying on the properties of southern pine poles. Part II: Chemical properties. Forest Prod J 19(2):37-43.

Wangaard FF (1966) Resistance of wood to chemical degradation. Forest Prod J 16(2):53-64.

Winandy J, Lebow P (2001) Modeling strength loss in wood by chemical composition . Part I. An individual component model for southern pine. Wood Fiber Sci 33(2):239-254.

CHAPTER VII

CONCLUSIONS AND RECOMMENDATIONS

This dissertation encompassed several studies describing the effects of wood modification by a partial hydrolysis on three hardwoods' mechanical, physical, surface, durability, and chemical properties. The fundamental hypothesis was that value can be added to the lignocellulosic ethanol conversion process by only partially hydrolyzing underutilized hardwood species, with the modified, yet structurally whole, wood byproduct being a desirable wood composite raw material. Red oak, sweetgum, and yellow-poplar were treated at 150°C for 30 minutes in three solutions, 1% sulfuric acid, water, and 1% sodium hydroxide. The results were compared with untreated controls from each species. To provide a bioenergy resource as well as a wood composite raw material, a partial hydrolysis would need to 1) lower both mass and specific modulus (SM), 2) increase the surface energy, and 3) separate a significant amount of wood sugars for ethanol conversion while 4) maintaining or improving the woods' biological durability.

Hardwood Species

Red Oak

Treating red oak in a strong acid or base at low concentrations provided good initial results, with modulus of elasticity (MOE) decreasing over 50%; water essentially had no effect as MOE increased slightly, 0.08%. There was less mass lost in red oak versus the other species. Upon oven-drying, specific gravity increased in all treatments compared to the control while MOE was only lowered in the acid treatment. Only the acid treatment showed a significantly lower SM than the control; all others were not statistically different. Surface energy, though, was improved by all treatments with water providing the highest value. Overall, red oak was more termite resistant than the other species, possibly due to the density and/or the anatomical structure of the species. A significant amount of holocellulose in red oak was removed by the partial hydrolysis treatment. The holocellulose content accounted for a significant amount of the variation in explaining mass loss due to treatment, specific modulus, and termite resistance.

Sweetgum

Sweetgum produced the highest initial decrease in MOE in each solution, a significantly higher mass loss, and consistently lower SM values across the treatments while its termite resistance was as good as red oak's and significantly better than yellow-poplar's. Surface energy values were comparable to the other species for each treatment. The SM results within sweetgum were not significantly different. The acid and water treatments increased the surface energy, with acid being the higher of the two. The alkaline treatment lowered the surface energy. Within each treatment sweetgum's mass

loss due to termite degradation was less than 10% versus its controls while red oak and yellow-poplar both experienced mass losses of over 20% in water and NaOH when compared with their controls. All treatments significantly reduced the carbohydrate content. Sweetgum was the most sensitive to the partial hydrolysis treatments as a higher percentage of holocellulose was extracted in all solutions compared with the other two species, likely due to the high concentration of pentosan hemicelluloses.

Yellow-poplar

A water treatment initially resulted in a significant increase in MOE of 11.7%. Only the base treatment provided an MOE decrease above 50%. Mass loss due to the treatments was significantly less than sweetgum's but similar to red oak. At the oven-dry condition, the MOE values for the treated samples were all less than the controls, but the specific gravity increased in the water and base treatments. Only an alkaline treatment provided a significantly lower SM, while all others were not statistically different as compared to the control. The surface energy values for yellow-poplar were higher than those for the other species in all treatments, except for the water treatment. The yellow-poplar/acid combination provided the highest overall surface energy. A basic treatment lowered the surface energy compared with the control. Yellow-poplar was significantly more susceptible to termite degradation, with an overall mass loss nearing 85%. All treatments extracted a significant amount of holocellulose. A strong relationship was found between holocellulose content and termite resistance, likely due to the high rate of activity within the species.

Treating Solutions

Acid

Experiments concluded that treating these southern species in a strong acid at low concentrations produced the greatest mass loss and increased surface energies across all three species. The MOE also decreased across all species, but specific gravity increased in red oak. When applying SM to eliminate the density effect across the species, an acid treatment gave inconsistent results. Yellow-poplar's SM increased compared to its control. While SM is a good indicator to reduce the density variation effect among the test specimens, its inherent weakness is that it overestimates when specific gravity is low, and underestimates when specific gravity is high. Acid treatments reduced the holocellulose content at least 10% in all species. The wood of acid-treated samples was extremely brash and friable following the partial hydrolysis, which could lead to plugging issues during mat formation.

Water

It can be concluded from laboratory tests that treating hardwoods in a heated water solution produced 1) a significant mass loss, 2) a decreased specific modulus, and 3) an increased surface energy across all species. Water was the only treatment that produced desirable results in all testing, with the exception of termite resistance as all treatments made the woods more susceptible to termite attack. Holocellulose content was significantly reduced in all species versus the controls.

Base

Treating the three species in a strong base at low concentrations did not produce optimum results. Only the goal of a significant mass loss was achieved. Holocellulose content was significantly reduced with mean MOE initially decreasing over 50% in all species following the partial hydrolysis treatment. Drying densified the woods as specific gravity increased in all species, and MOE increased in red oak and sweetgum. Only yellow-poplar's SM was significantly lower than its control. Additionally, the surface energies of treated sweetgum and yellow-poplar decreased versus the controls. Termite resistance was significantly compromised by the alkaline treatment, though not statistically different from the water treatment.

Recommendations

Results suggest further investigating the modification of sweetgum wood for composites manufacturing. From a forest management perspective, sweetgum is the single-most populous hardwood species in the South. While valuable wood products from veneer and sawlog grade timber can be processed from the wood, it is often looked upon as an undesirable species and eliminated during early release silvicultural treatments. Significant mass losses coupled with carbohydrate reductions of almost 15% imply that this species can be successfully utilized for wood sugar harvesting. Also, while there was no "silver bullet" treatment for sweetgum, it did not appear anything detrimental occurred mechanically, physically, or to the wood surface. Pilot scale manufacturing and quality control testing should be conducted on varying levels of treated and untreated sweetgum flakes mixed with southern pine.

From a practical standpoint, water is the most economical and environmental choice for carrying out a partial hydrolysis. From statistical processing control perspective, it is also a better choice as proven by the consistent results in this dissertation. While termite resistance was decreased, this could possibly be overcome by manufacturing a densified composite product. Field tests will need to be conducted for confirmation and can be expanded to include fungal durability. Chemical analyses should be expanded to investigate lignin, alpha cellulose, and ash content to determine their contribution to predicting wood properties.

An ad hoc follow-up test was conducted on sweetgum treated in a heated water solution at varying times and temperatures to help guide future research. Three replicates treated for 30 and 60 minutes at two temperatures, 145 and 175°C, were investigated. Treating methodology followed the same procedures as prior chapters. The MOE and dynamic contact angle (DCA) in pMDI, a commonly used resin in the wood composites industry, were investigated by analysis of variance. Results indicated a longer treatment time or a higher treating temperature independently and significantly lowered mean MOE; however, neither treatment time nor temperature had a significant effect on mean DCA.

A multivariate analysis of variance (MANOVA) was then run to determine the interrelationships of these effects. The MOE and DCA did not correlate ($r = 0.26$), and MANOVA showed no significant overall treatment effect on the responses (Wilks lambda, $\lambda=0.22$, $p = 0.06$). Thus, treating at higher temperatures and/or longer treatment times may not impart any added significance to the wood's overall suitability for composite production. In fact, shorter treatment times, i.e. < 30 minutes, and lower

temperatures near, or at, the threshold for hemicellulose extraction, 140°C, may still provide significant differences between untreated and treated wood material.

This rudimentary test should expanded to include other manufacturing steps, such as strand thickness, alignment, drying, resin and additives, and press cycling, so that costs are kept to a minimum while providing added value to the extraction process. Comprehensive testing of pressed panels or billets should also take place. Economic analyses need to be conducted at each stage of production forestry to determine the viability of the fundamental hypothesis for this research.

APPENDIX A

ADVANCING CONTACT ANGLES OF THE WOOD/TREATMENT COMBINATIONS IN FOUR PROBE LIQUIDS

Probe Liquid

Advancing contact angle (standard deviation)

Treatment Combination	Formamide	Water
Red Oak/Acid	25.0 (23.9)	80.6 (6.3)
Red Oak/Water	37.4 (6.4)	49.9 (10.0)
Red Oak/Base	46.5 (5.1)	51.0 (6.7)
Red Oak/Control	43.6 (1.7)	64.0 (10.0)
Sweetgum/Acid	9.0 (15.4)	80.0 (5.9)
Sweetgum/Water	37.1 (6.67)	50.2 (3.8)
Sweetgum/Base	45.9 (6.7)	55.6 (2.9)
Sweetgum/Control	38.8 (3.7)	51.0 (14.3)
Yellow-poplar/Acid	3.9 (9.6)	52.8 (15.4)
Yellow-poplar-Water	30.8 (5.9)	48.3 (12.0)
Yellow-poplar/Base	42.9 (5.0)	54.8 (13.0)
Yellow-poplar/Control	32.4 (3.8)	48.4 (10.3)

Probe Liquid

Advancing contact angle (standard deviation)

Treatment Combination	α-Bromonapthalene	Ethylene glycol
Red Oak/Acid	29.9 (11.6)	19.3 (17.8)
Red Oak/Water	28.3 (7.0)	32.4 (4.8)
Red Oak/Base	37.9 (8.2)	39.9 (7.3)
Red Oak/Control	36.6 (6.2)	39.2 (2.9)
Sweetgum/Acid	13.0 (14.7)	8.1 (11.4)
Sweetgum/Water	30.6 (5.4)	36.5 (6.6)
Sweetgum/Base	37.9 (5.1)	40.0 (5.9)
Sweetgum/Control	31.7 (8.6)	36.3 (3.6)
Yellow-poplar/Acid	0.0 (0.0)	0.0 (0.0)
Yellow-poplar-Water	16.6 (12.3)	26.0 (10.9)
Yellow-poplar/Base	32.0 (11.1)	35.0 (4.9)
Yellow-poplar/Control	30.3 (4.8)	37.1 (3.4)