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DECAY AND ENVIRONMENTAL STUDIES ON SOUTHERN PINE

By

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DECAY AND ENVIRONMENTAL STUDIES ON SOUTHERN PINE

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This work focused on decay and dimensional stability of southern pine lumber and environmental issues associated with emissions released during kiln drying of southern pine.

In one study decking boards were treated with a 3% resin acid solution to increase the dimensional stability.  The boards were placed on a roof and weathered for two years. The increased water repellency reduced moisture gain following summer rainstorms by one-third compared to untreated matched samples, this significantly reduced splitting by half and cupping by one-third.

In one study decking boards from matched samples were weathered for two years in the roof setup described above, and in a fungal ground proximity test.  The ground proximity samples had slightly more decay than the roof samples.  Correlation between decay ratings for the matched samples was 37%, suggesting above-ground decay susceptibility is dependent on the macro- and micro-environment.  Decay in roof exposure was modeled based on moisture content factors, whereas decay in ground proximity was modeled by the resin and fatty acids.

One study tested pole sections with varying amounts of sapwood, heartwood, and knots dried in a pilot-scale kiln. A sample of the kiln exhaust was measured for volatile organic compounds. Emissions from poles were similar to clear lumber. Emissions from heartwood poles were less than for heartwood lumber, perhaps due to the poles' sapwood band.

The final study was conducted with clear and knotty lumber kiln dried to below 8% moisture content using three kiln schedules. Wood dried to this lower moisture content is used in interior applications or exported. During drying, a sample of the kiln exhaust was analyzed for total VOCs, and a sample of the kiln exhaust was collected and analyzed for hazardous air pollutants via gas chromatography and spectrophotometry. For all three kiln schedules, mills would reach 10 tons of methanol and thus must comply with maximum achievable control technology standards before reaching 25 tons of methanol, formaldehyde, acetaldehyde, acrolein, and propionaldehyde.

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# CHAPTER I

## INTRODUCTION

### Background

Southern pine (SP) accounts for 44% of the softwood lumber production in the United States (Howard 2001).  Southern pine is used in many different applications including as a feedstock for paper, structural lumber, treated wood products including decking, utility poles and marine pilings, as well as flooring, paneling, and composite wood products (Wiemann 2010).

Wood can shrink or swell unevenly which can result in dimensional instability (Hoadley 2000).  Wood is also an organic material and is susceptible to biological deterioration from fungi, insects, bacteria and marine borers (Clausen 2010).  To protect wood from biological attack preservative treatments are used to extend the service life of wood products (Lebow 2010).

Volatile organic compounds (VOCs) and hazardous air pollutants (HAPs) are released from SP during kiln drying.  Volatile organic compounds react with nitrogen oxides ($NO_x$) in the presence of ultra-violet (UV) light to form ground level ozone ($O_3$), a major component of smog (EPA 1998).  Hazardous air pollutants (HAPs) are known or suspected carcinogens or have other serious health effects.  Some HAPs can be produced during the processing of wood.

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## Objective Statement

The objectives of the study focused on two important areas of SP research: decay and dimensional stability in above-ground environments and environmental issues associated with emissions released during kiln drying of wood. Two studies were conducted in each area.

In the first decay study flatsawn and quartersawn SP decking boards were treated with a 3% resin acid waterborne solution to increase the dimensional stability. The boards were placed on a roof top in Starkville, Mississippi and weathered for two years. The boards were rated for moisture uptake, splitting, and cupping before and after summer rainstorms to determine if the resin acid system was effective versus the untreated matched control samples.

The second decay study examined the decay susceptibility of SP boards over two years in two above-ground locations, the roof setup described above, and a standard ground proximity test that encourages fungal growth. The roof samples were frequently weighed before and after rain to determine estimated moisture content gain, and periodically rated for checking and decay. The ground proximity samples were also periodically rated for decay. After two years of exposure the samples were cut into sections to better observe interior decay and rated for decay one final time. The extent of decay was then modeled based on the permeability, the average amount of water absorbed during rainstorms (rain absorption), the check rating, the mold rating, the amount of individual fatty and resin acids, the soluble sugar content, the oven dry weight (density) of the sample, and the rings per inch (growth rate).

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In the first environmental study SP pole sections with varying amounts of sapwood, heartwood, and knots were obtained from a local pole manufacturer. These sections were kiln dried in a pilot-scale kiln with a high temperature pole schedule. During drying a sample of the kiln exhaust was analyzed for total VOC emissions. The results were compared to previous studies on lumber to determine how different pole emissions are from lumber and thus how appropriate it is to use emissions from lumber to permit pole facilities.

The second environmental study was conducted with clear and knotty SP lumber kiln dried to below 8% moisture content using an elevated kiln schedule and two high temperature kiln schedules. Products dried to below 8% moisture content are used in interior applications such as flooring and paneling or exported. The time required to kiln dry from green to below both 19% and 8% moisture content was recorded to facilitate comparison to previous studies and to determine the additional release of emissions when drying to below 8% moisture content. During drying, a sample of the kiln exhaust was analyzed for total VOCs, and a sample of the kiln exhaust was collected and analyzed for HAPs via gas chromatography and spectrophotometry. Formaldehyde, methanol, acetaldehyde, acrolein, and propionaldehyde were the HAPs targeted for analysis. If emissions of HAPs are over 10 tons per year of a single compound or over 25 tons per year of overall compounds then a facility will be regulated under the maximum achievable control technology standards.

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# Literature Cited

Clausen, C.A. 2010.  Biodeterioration of Wood.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

Environmental Protection Agency (EPA).  1998  NOx:  How Nitrogen Oxides affect the way we live and breathe.  Office of Air Quality, Planning, and Standards.  Research Triangle Park, NC.  6 pp.

Hoadley, R.B.  2000.  Understanding Wood: A Craftsman's Guide to Wood Technology.  Taunton Press, Inc.  Newton, CT. 280 pp.

Howard, J.L.  2001.  U.S. timber production, trade consumption, and price statistics 1965 to 1999.  Res. Pap.  FPL-RP-595.  Madison, WI:  U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.  90 pp.

Lebow, S.T. 2010.  Wood Preservation.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

Wiemann, M.C. 2010.  Characteristics and availability of commercially important woods.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

CHAPTER II

LITERATURE REVIEW

**Southern Pine**

Southern pine (SP) is composed of four major species; loblolly (*Pinus taeda* L.), short-leaf (*Pinus echinata* M.), long-leaf (*Pinus palustris* M.), and slash pine, (*Pinus elliottii* E.) as well as five minor species (Neubrech 1939). Wood from these trees is categorized and graded as SP because of their similar anatomy and physical properties (Wiemann 2010). The lumber from these trees is the strongest and densest amongst the commonly used softwoods that grow in the United States (Hoadley 1993). The specific gravity of SP typically averages between 0.51 and 0.61 (Hoadley 1993). Southern pine is used in many different applications including as a feedstock for paper, structural lumber, treated wood products including decking, utility poles and marine pilings, as well as flooring, paneling, and composite wood products (Wiemann 2010).

Southern pine trees range primarily in the southeastern United States, i.e. from east Texas to the Atlantic coast and north to southern Virginia and Kentucky (Wear and Greis 2002). These states account for 58% of the timber production in the United States (SFPA 2005), and they collectively produce more forest-related products than any single foreign country (Wear and Greis 2002). Southern pine is the primary species group harvested from the South, with production totaling approximately 18 billion board feet in

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2004 (SPC 2005).  Southern pine accounts for 44% of softwood lumber production in the United States (Howard 2001).

In 1997, SP grew on over 62 million acres in the United States on both natural and plantation stands (South and Buckner 2003).  In 1952, the southeastern region accounted for approximately 41% of lumber production while the pacific region accounted for approximately 38% of lumber production.  In 1997, production in the pacific region decreased to 18% while production in the southeastern region increased to 58%. (Prestemon and Abt 2002).  While forest-based production continues to shift to the southeast, the total amount of SP acreage decreased by 16 million acres since 1953, primarily due to urbanization (South and Buckner 2003).  To meet the increased demand for forest products, high-production plantation grown trees accounted for 32 million acres in 1999 (Prestemon and Abt 2002).

## Wood Drying

Water typically constitutes roughly half of the weight of freshly sawn, green lumber (Bowyer et al. 2007).  Liquid water and vapor water reside within the cell lumen and the cell wall is saturated with bound water in green lumber.  During wood drying, all of the liquid water is removed from the cell lumen while some water vapor still remains within the cell lumen and some bound water still remains in the cell wall (Figure 2.1). (Bowyer et al. 2007).  Wood is dried from approximately 100% moisture content (MC) (dry basis) to below 19% MC for softwood lumber, and between 6% to 8% MC for hardwood lumber (Bowyer et al. 2007).  Advantages to drying lumber include reduction of weight for shipping and handling purposes, avoiding in-service shrinking and swelling,

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reduction of attacks from mold, fungi, and insects, increased strength properties, ease of application of wood preservatives, and customer satisfaction (Henderson 1951).
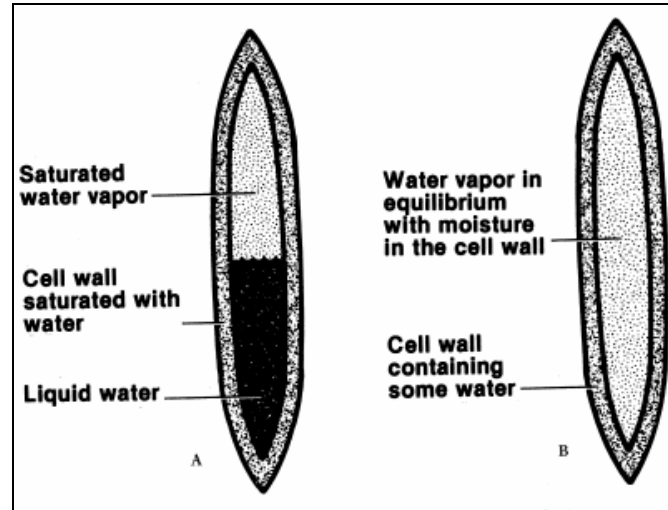


Figure 2.1    Water in a cell of green wood (A); water in a cell of dry wood (B)
              (Bowyer et al. 2007)

The fastest practical method of drying lumber is through kiln drying. Softwood lumber is typically dried in compartment kilns (Simpson 1991). Compartment kilns often have charges loaded into the kiln via tracks and the charges remain stationary during the drying process. In 1993, there was an estimated 2500 lumber dry kilns used to dry SP lumber in the United States (Sellers 1993).

Softwood kilns usually use steam (indirect heat) or combustion gasses (direct heat) to heat the air to high temperatures where it is passed through stacked lumber via a series of fans (Simpson 1991). Water is vaporized from the wood surface into the air. As the water evaporates from the surface of the wood into the air, water migrates from the inside of the wood to the surface of the wood. (Henderson 1951). The rate of drying in the wood is determined by the physical properties of the wood, the wood MC, the

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dimensions of the wood, and the drying conditions.  The drying conditions are controlled with the air flow rate of the kiln, the velocity of the fans, the dry and wet bulb temperatures, and the size of the lumber charges (Koch 1972).  As the wet bulb temperature, and hence the moisture in the air increases in the kiln the air is exhausted through vents and new dry air is circulated in.  The physical properties of the wood dictate how fast the water moves from the inside of the wood to the surface.  The ideal situation is the removal of water from the surface of the lumber at the same rate at which water moves from the inside to the surface of the lumber (Wilkinson 1979).

Different wood species dry at different rates.  For example, SP dries quickly while red and white oak dry very slowly due to slow moisture movement from the interior of the wood to the surface.  Kiln schedules are used to control the proper amount of drying in wood.  The industry categorizes kiln schedules into four types, low, conventional, elevated, and high-temperature (Simpson 1991).  A low-temperature dry kiln operates between 21°C and 49°C.  A conventional-temperature dry kiln operates between 43°C and 82°C.  An elevated-temperature kiln operates between 82°C and 99°C.  A high-temperature kiln operates above 100°C, typically extending to 138°C (Simpson 1991).  The majority of southern pine is dried in high-temperature dry kilns, while the majority of hardwood lumber is dried in conventional-temperature kilns.


**Wood Properties – Shrinking and Swelling**

When bound water is removed or added to the cell wall shrinking and swelling occurs (Bowyer et al. 2007).  The shrinking and swelling process stresses wood cells and when the stress exceeds wood's perpendicular-to-grain strength checking or separation of

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the cells along the grain occurs (Figure 2.2) (Hoadley 2000).  Wood is an anisotropic

material (Figure 2.3) and will warp when shrinkage or swelling occurs unevenly

(Hoadley 2000).  Tangential shrinkage is typically double that of radial shrinkage;

longitudinal shrinkage is typically 0.1% to 0.2% (Hoadley 2000).



Figure 2.2      Surface checking on flatsawn southern pine lumber

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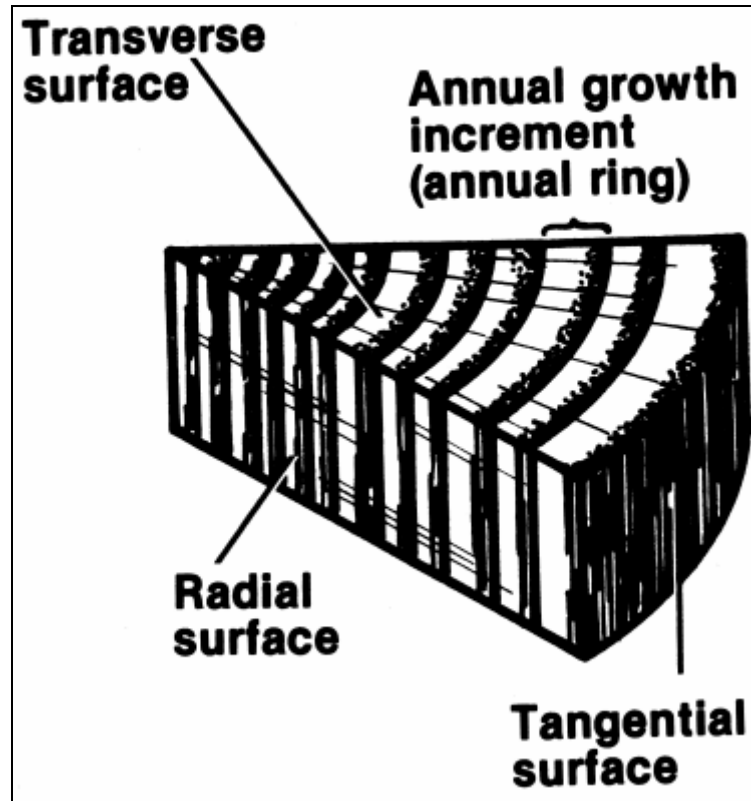
Figure 2.3    The three surfaces of wood (Boywer et al. 2007)

**Biodeterioration and Wood Preservation**

Wood is an organic material and thus susceptible to biological deterioration from fungi, insects, bacteria and marine borers (Clausen 2010).  Wood dried to below 20% MC that is not exposed to additional water will be free from advancing decay (Clausen 2010). While some species of wood have naturally durable heartwood and thus are appropriate for exterior use many do not and sapwood from all species is susceptible to decay (Clausen 2010).  To protect wood from biological attack preservative treatments are used to extend the service life of wood products (Lebow 2010).  The two common types of wood preservatives are oil-soluble compounds and waterborne salts (Bowyer et al. 2007). Currently 19 million cubic meters of wood is treated each year (SFPA 2005;

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Micklewright 1998).  Common oil-borne preservatives are creosote and

pentachlorophenol.  Waterborne preservatives include chromated copper arsenate (CCA),

ammoniacal copper quat (ACQ), micronized copper quats (MCQ), and others.  Generally

wood preservatives are becoming more environmentally friendly and research is being

conducted on combinations of organic compounds (Schultz and Nicholas 2000).

## Extractives

A small fraction, by weight, of the overall wood components is composed of

numerous organic compounds that are soluble in water or organic solvents; these

compounds are termed "extractives" (Sjostrom 1993).  Extractives are non structural

components that aid in insect and fungi protection, and provide a food source to a living

tree (Sjostrom 1993).  Southern pine typically contains approximately 2% to 10%

extractives (Panshin et al. 1950).  Extractives include terpenoids, flavonoids, lignans,

phenols, waxes, fats, sugars, and resin acids (Obst 1998).  Resin acids are recovered

during the kraft pulping of pines by skimming the tall oil from the black liquor recovery

and extracting with sulfuric acid.  Approximately 50 kg of resin acids can be obtained

from 1 ton of pulp (Sjostrom 1993).  Common resin acids extracted from pulping include

pimaric, sandaracopimaric, isopimaric, dehydroabietic, levopimaric, palustric, abietic,

and neoabietic resin acids (Holmbom 1978).

The terpenoids are the largest component of SP extractives and are composed of

isoprene units composed of five carbon and eight hydrogen atoms (Figure 2.4; Figure

2.5) (Sjostrom 1993).  Terpenoids can be used in a variety of products including

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fragrances, insect repellents, medicine, flavoring agents, and waterproofing materials (Obst 1998). Terpenes are found in resin canals (Sjostrom 1981).
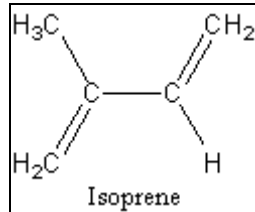


Figure 2.4     Single isoprene molecule
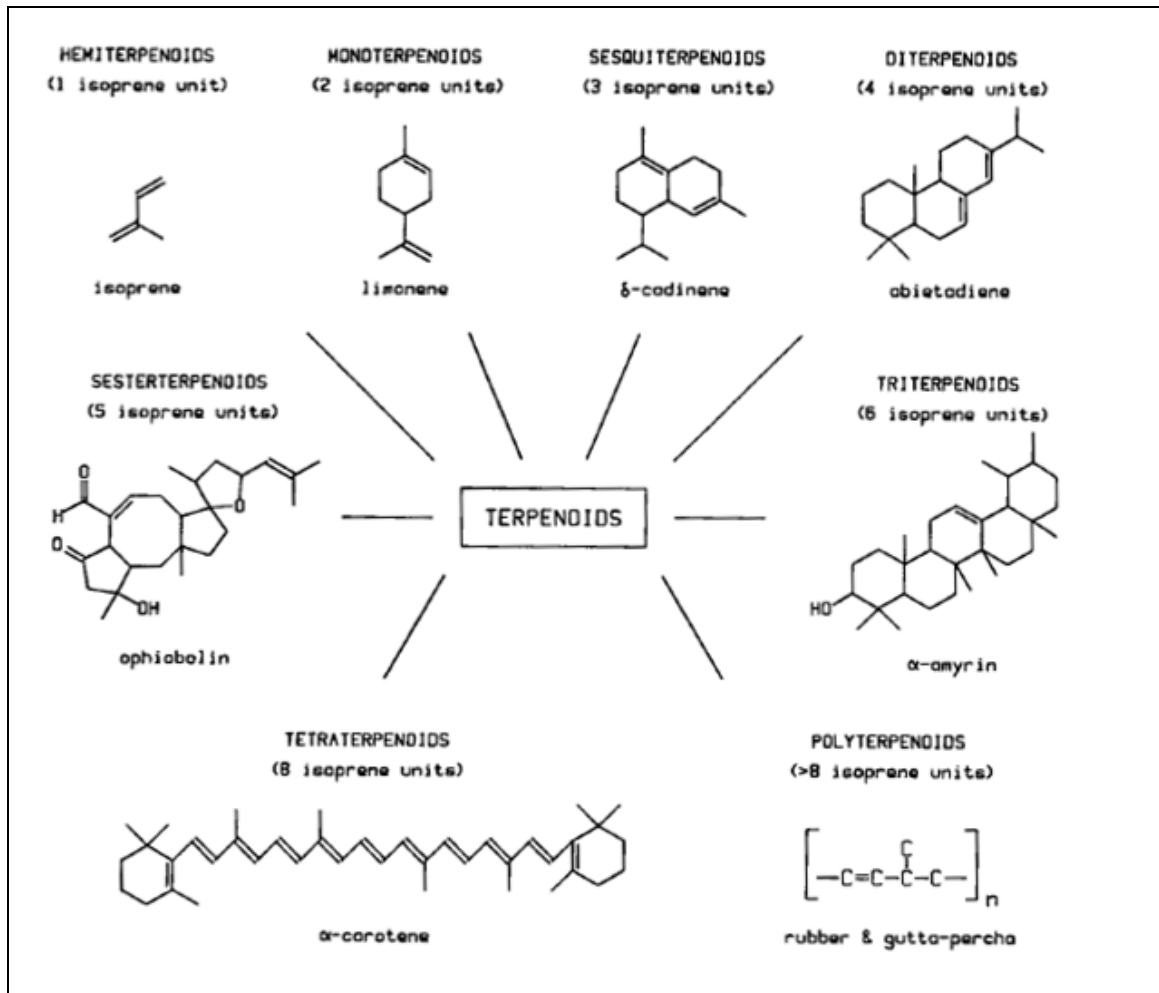


Figure 2.5     Terpenoids (Zavarin and Cool 1991)

Monoterpenes are composed of two isoprene units and are the primary chemicals volatilized during SP drying (Koch 1972). α-Pinene and β-pinene are monoterpenes that respectively account for approximately 64% and 28% of the terpenes in loblolly pine (Drew and Pyland 1966). Other monoterpenes include camphene, limonene, and myrcene (Figure 2.6). Estragole (P-allylanisole) is also commonly found in SP. The relative amount of terpenes differs in regards to the heartwood and sapwood regions of the tree. In a study of terpene composition, heartwood in loblolly pine was found to have an average terpene composition of 2.3%, while inner sapwood had 0.77% and outer sapwood was composed of 0.35% terpenes (Thompson et al. 2005).
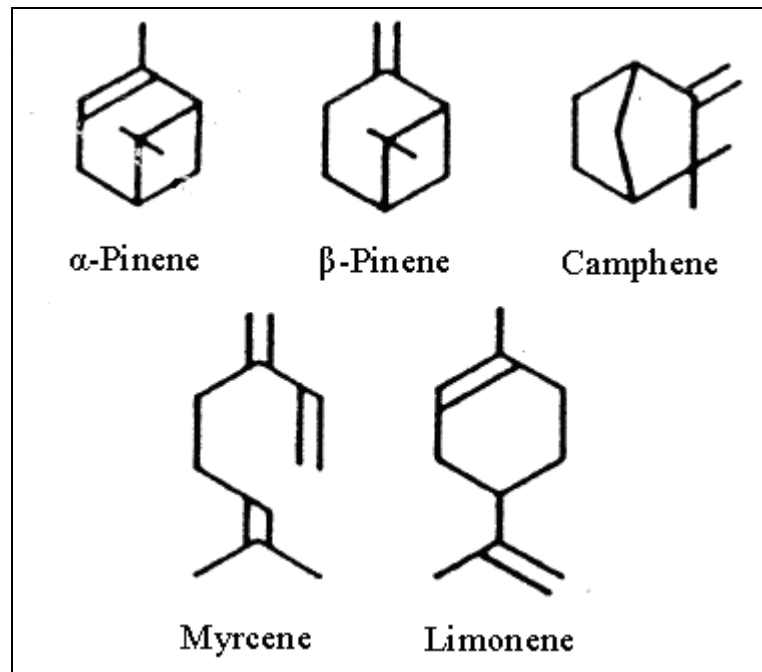


Figure 2.6    Common monoterpenes in southern pine

Terpenes volatilize during drying due to their relatively low molecular weight and high vapor pressure (Banerjee et al. 1998). The volatilization of these oils result in air

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pollution (Obst 1998). These pollutants are broadly referred to as volatile organic compounds (VOCs) (Emery 1991). Volatile emissions from SP lumber average between 3 and 4 pounds of VOCs emitted per 1,000 board feet (MBF) of lumber during kiln drying (Milota 2000).

Volatile organic compounds are emitted into the environment both naturally and through human related activities. While many VOCs occur naturally, the rate of emissions has increased substantially since 1900 due to human activities (Bailey 2000). Terpenes can form as well as react with ozone ($O_3$) (NRC 1991). Ozone is formed when VOCs react with nitrogen oxides ($NO_X$) in the presence of ultra-violet light; ozone can lead to lower plant growth and can cause human respiratory problems (EPA 1998).

### Clean Air Act and Permit System

The emissions released during wood drying are regulated by the Clean Air Act which was last amended in 1990. The act and amendments give authority to the Environmental Protection Agency (EPA) to set consistent national standards for air pollutants.

Ozone is one of six criteria pollutants that are regulated under the National Ambient Air Quality Standards (NAAQS). The NAAQS exist to protect public health, animals, and the environment (Salzman and Thompson 2003). The maximum safe level of ozone determined by the EPA is 0.08 parts per million (ppm) over eight hours (Kubasek and Silverman 2004). The EPA estimated in 2005 that 98 million people live in regions where pollution levels exceed the ozone standards (EPA 2009b). The NAAQS

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eliminates the ability of states to allow industrial and economic growth by sacrificing environmental quality (Salzman and Thompson 2003).

When a region has a criteria pollutant that exceeds the maximum safe level the region is considered to be in non-attainment for that pollutant (Kubasek and Silverman 2004). While in non-attainment status, the state and local governments have the authority to enforce reduced emission levels for both point-source and non point-sources of the pollutant (Kubasek and Silverman 2004). The level of non-attainment in areas is categorized as marginal, moderate, serious, severe, and extreme (Salzman and Thompson 2003). Areas of ozone non-attainment over eight hours are shown in Figure 2.7.
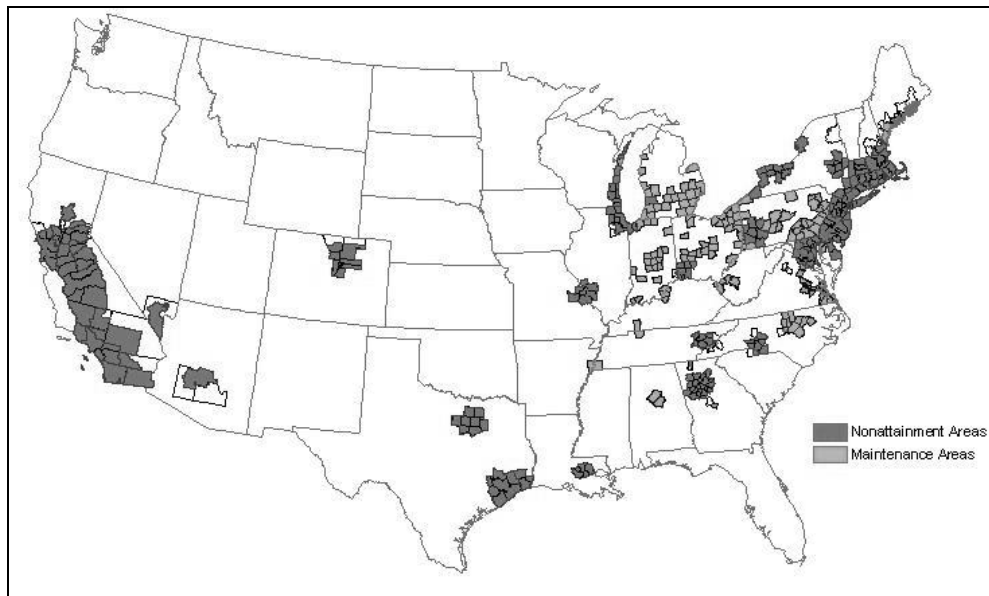


Figure 2.7    Eight hour ozone non-attainment in the United States (EPA 2010)

Each state develops State Implementation Plans (SIP) for assessing and attaining air quality for meeting the NAAQS (Kubasek and Silverman 2004). If an area of the country meets or exceeds the NAAQS levels, the region must not have No Significant

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Deterioration (NSD) in their air quality (Kubasek and Silverman 2004). The program complies with the Clean Air Act in regards to protecting and enhancing the air quality (Salzman and Thompson 2003).

The permitting system establishes guidelines on the amount of pollutants that point- and non-point sources can emit over a five year period (Kubasek and Silverman 2004). A stationary source must have a permit if more than 100 tons of pollutants, 25 tons collectively for all hazardous air pollutants (HAPs), or 10 tons of any single HAP is released per year (Salzman and Thompson 2003). Exposure to HAPs can result in chronic and acute illness, cancer, diseases of the respiratory system, and other serious health effects (Vig and Kraft 2006). If the amount of chemicals emitted from a source is more than these levels, the EPA will put forth a standard of maximum achievable control technology (MACT) for the HAPs released (Kubasek and Silverman 2004). Enforcement of these permits is at the local and state level. Since 1990 HAP emissions have decreased 42% and VOCs have decreased 31% (EPA 2009a).

## Literature Cited

Bailey, R (ed).  2000.  Earth Report 2000.  McGraw-Hill Book Company.  New York, NY.  362 pp.

Banerjee, S., W. Su, L.P. Otwell, M.E. Hittmeier, and K.M. Nichols.  1998.  Wet line extension reduces VOCs from softwood drying.  Environmental Science and Technology 32:1303-1307.

Bowyer, J.L., R. Shmulsky, and J.G. Haygreen.  2007.  Forest Products and Wood Science:  An Introduction.  Iowa State University Press.  Ames, IA.  558 pp.

Clausen, C.A. 2010.  Biodeterioration of Wood.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

Drew, J., and G. Pylant, Jr. 1966.  Turpentine from pulpwoods of the United States and Canada.  Tappi Journal.  Vol. 49, No. 10.  pp. 430-438.

Emery, J.  1991.  Chemicals Released from Wood During Drying.  National Particleboard Association, America Plywood Association Pollution Control Technology Seminars.  National Particleboard Association, Gaithersburg, Maryland.  pp. 9 – 10.

Environmental Protection Agency (EPA).  1998  NOx:  How Nitrogen Oxides affect the way we live and breathe.  Office of Air Quality, Planning, and Standards.  Research Triangle Park, NC.  6 pp.

Environmental Protection Agency (EPA).  2009a  Air Emissions Summary Through 2005.  Accessed July 19, 2010.  http://www.epa.gov/airtrends/2006/emissions_summary_2005.html

Environmental Protection Agency (EPA).  2009b  Air Quality Summary Through 2005.  Accessed July 19, 2010.  http://www.epa.gov/airtrends/2006/aq_summary_2005.html

Environmental Protection Agency (EPA).  2010  Nonattainment and Maintenance Areas in the U.S. 8-Hour Ozone Map.  Accessed July 19, 2010.  http://epa.gov/airquality/greenbk/map8hrnm.html

Henderson, H.L.  1951.  The Air Seasoning and Kiln Drying of Wood.  Albany, New York.  364 pp.

Hoadley, R.B.  1993.  Identifying Wood:  Accurate Results With Simple Tools.  Taunton Press, Inc.  Newton, CT. 224 pp.

Hoadley, R.B.  2000.  Understanding Wood: A Craftsman's Guide to Wood Technology. Taunton Press, Inc.  Newton, CT. 280 pp.

Holmbom, B. 1978.  Constituents of tall oil.  A study of tall oil processes and products. Diss., Abo Akademi, Abo.

Howard, J.L.  2001.  U.S. timber production, trade consumption, and price statistics 1965 to 1999.  Res. Pap.  FPL-RP-595. Madison, WI:  U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.  90 pp.

Koch, P.  1972.  Utilization of Southern Pines.  U.S. Department of Agriculture Forest Experiment Station, Agriculture Handbooks No. 420. pp 1-51.

Kubasek, N.K. and G.S. Silverman.  2004.  Environmental Law.  Pearson Prentice Hall. Upper Saddle River, New Jersey.  pp. 466.

Lebow, S.T. 2010.  Wood Preservation.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

Micklewright, J.T. 1998.  Wood Preservation Statistics-1997.  American Wood Preservation Association.

Milota, M.R.  2000.  Emissions From Wood Drying:  The Science And The Issues. Forest Products Journal.  50(6):10 – 20.

National Research Council (NRC).  1991.  Rethinking the ozone problem in urban and regional air pollution.  National Academy, Washington, DC. pp. 1-208.

Neubrech, W. L.  1939. American Southern Pine.  Washington: United States Government Printing Office, 36 pp.

Obst, J.R.  1998.  Forest Products Biotechnology – Special (Secondary) Metabolites from Wood.  Taylor and Francis Inc.  Bristol, PA.  pp. 151 – 166

Panshin, A.J., E.S. Harrar, W.J. Baker, and P.B. Proctor.  1950.  Forest Products:  Their Sources, Production, and Utilization.  McGraw-Hill Book Company.  New York, NY. 540 pp.

Prestemon, J.P., and R.C. Abt.  2002.  The Southern Forest Resource Assessment – Timber Products Supply and Demand.  Gen. Tech. Rep. SRS-54. Asheville, NC:  U.S. Department of Agriculture, Forest Service, Southern Research Station and Southern Region. 28pp.

Salzman, J. and B.H. Thompson, Jr. 2003.  Environmental Law and Policy.  Foundation Press.  New York, New York.  pp. 305.

Schultz, T.P. and D.D. Nicholas.  2000.  Naturally durable heartwood: Evidence for a proposed dual defense function of the extractives.  Phytochemistry. 54:47-52.

Sellers, T., Jr.  1993.  Estimated Production and Number of Mills for Southern Pine Lumber:  Kilns and Wood-Based Composites in the United States.  Mississippi State University, Forest Products Laboratory (Report).  Mississippi State, MS.

Simpson, W.T. 1991.  Dry Kiln Operators Manual.  U.S. Department of Agriculture, Forest Service, Forest Products Laboratory.  Madison, WI.  274 pp.

Sjostrom, E.  1993.  Wood Chemistry Fundamentals and Applications.  Academic Press, Inc., New York, NY.  293 pp.

South, D.B., and E.R. Buckner.  2003.  The Decline of SYP Timberland.  Journal of Forestry.  January / February 2003.  pp. 30-35.

Southern Forest Products Association (SFPA). 2005.  Industry statistics, southern pine treated production.  Kenner, Louisiana: Southern Forest Products Association.

Southern Pine Council (SPC). 2005.  Southern Forest Facts.  Accessed: August 16, 2005.  < http://www.southernpine.com/forestfacts.shtml >

Thompson, A., J. Cooper, and L.L. Ingram, Jr.  2005.  Distribution of Terpenes in Heartwood and Sapwood of Loblolly Pine.  Forest Products Journal Vol. 56, No. 7/8.  pp. 46 – 48.

Vig, N.J., and M.E. Kraft.  2006.  Environmental Policy from the 1970s to the Twenty-First Century.  In N.J. Vig and M.E. Kraft (Eds).  Environmental policy: new directions for the twenty-first century.  CQ Press, Washington, DC.

Wiemann, M.C. 2010.  Characteristics and availability of commercially important woods.  In Robert J. Ross (Eds.).  Wood Handbook: Wood as an Engineering Material.  United States Department of Agriculture: Forest Service.  General Technical Report: FPL-GTR-190.

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Wear, D. N., and J.G. Greis.  2002.  The Southern Forest Resource Assessment - Summary Report.  Gen. Tech. Rep. SRS-54. Asheville, NC:  U.S. Department of Agriculture, Forest Service, Southern Research Station and Southern Region. 114pp.

Wilkinson, J.  1979.  Industrial Timber Preservation.  Associated Business Press, London England.

Zavarin, E., and L. Cool.  1991.  Wood Structure and Composition:  Extraneous Materials from Wood.  Marcel Dekker, Inc.  New York, NY.  pp. 321 – 407.

CHAPTER III

WATER REPELLENCY AND DIMENSIONAL STABILITY OF SOUTHERN PINE

DECKING TREATED WITH WATERBORNE RESIN ACIDS

**Abstract**

Many residential consumers prefer that wood used in above-ground exterior applications be protected by environmentally-benign biocide systems and have good dimensional stability. To help achieve these two properties resin acids, a by-product from the kraft pulping of pines, was employed in a waterborne formulation. In an extremely harsh above-ground exterior exposure, two sets of decking boards treated with the resin acid system had water repellent properties that were still effective after up to two years of exposure. The increased water repellency reduced the moisture gain following summer rainstorms by about one-third compared to untreated matched samples, and this was sufficient to significantly reduce splitting by about half and cupping by one-third. A wide variation in moisture gain following rain was observed for the untreated sapwood flatsawn decking samples, with the moisture gain positively and significantly correlated to the extent of checking. The optimal use of resin acids may be to provide some limited dimensional stability and, in combination with antioxidants and organic biocide(s), as a benign wood preservative system.

## Introduction

Wood products are used in residential construction and other outdoor applications where the wood can be biodegraded by many fungi and insects. To prevent deterioration, non-durable wood products can be treated with biocides. Wood preservation has recently undergone dramatic and rapid changes worldwide due to a demand for environmentally-benign residential wood preservative systems. Wood is also a hygroscopic material that in above-ground exposure such as decking will swell unevenly when wetted and then shrink as it dries. This dimensional instability often leads to undesired checking and warping in treated lumber (Preston 2000; Evans 2003; Vlosky and Shupe, 2004).

To address the above problems work has been done on developing environmentally-benign organic wood preservative systems and water repellents (Kabir et al. 1992; Schultz and Nicholas 2002; Schultz et al. 2005; Schultz et al. 2007a). The wood preservative systems combine organic biocides with non-biocidal, benign, and low-cost additives that enhance the biocides' efficacy, specifically antioxidants and metal complexing compounds. These additives were selected based on the fungal decay mechanisms and the properties of heartwood extractives. Specifically, extractives in naturally durable heartwood have excellent antioxidant and metal chelator properties (Schultz and Nicholas 2002), and antioxidants and metal complexing compounds interfere with the wood-degrading free radicals generated by fungal metal-mediated reactions (Goodell 2003; Henry 2003; Rodriquez et al. 2003; Schultz et al. 2005). Thus, the approach mimics natural durability. Furthermore, some extractives, such as terpenoids, are very hydrophobic and thus water repellents. Water repellents enhance the

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durability of treated wood products by reducing the decay potential and extent of biocide leaching, and further improve the dimensional stability of treated wood (Preston 2000; Preston 2003).

A non-leachable, economical and stable antioxidant, butylated hydroxytoluene or BHT, was identified that was effective in laboratory and outdoor studies (Schultz and Nicholas 2002; Schultz et al. 2005). A suitable metal complexing compound proved more difficult to select but a recent report showed that resin acids give enhanced efficacy when combined with organic biocides (Schultz et al. 2007b). Furthermore, when formulated into a waterborne system enhanced water repellency is obtained (Schultz et al. 2007a). Resin acids are a by-product from the kraft pulping of pines, are benign and inexpensive.

The objective of this study was to determine the change in moisture content (MC) over time in two sets of southern pine decking boards that had been treated with waterborne resin acids, then exposed in a harsh above-ground environment for at least a year. One set consisted of commercial nominal 5/4 flatsawn decking, and the second was laminated quartersawn samples of the same thickness. The laminated samples were produced because quartersawn lumber has good dimensional stability and fewer tendencies to check than flatsawn lumber. The moisture content changes were measured during the hot summer months in Mississippi where extremely high temperatures and often relatively low humidities alternating with short thunderstorms cause above-ground lumber to undergo rapid wet and dry cycles and thus result in undesired dimensional changes.

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**Materials and Methods**

The preparation and treatment of the southern pine samples were as previously described (Schultz et al. 2007a).  Briefly, one sample set was cut from commercial flatsawn 5/4 defect-free, untreated sapwood decking, each 112 cm long, 2.5 cm thick and 14 cm wide, which were then cut into two matched 65 cm long samples, one treated and one control (Figure 3.1).  A total of 12 replicate sets were prepared.  The samples were then weighed and the moisture content determined using a Wagner dielectric moisture meter so that the oven-dry weight could be estimated for later determination of the moisture content when outdoors.  The second set consisted of quartersawn laminated samples made by gluing defect-free southern pine flatsawn sapwood lumber together, then sawing the billets into 2.5 cm thick by 14.6 cm wide laminated quartersawn boards that were then cut to give three replicate samples each 33 cm long (Figure 3.2).  These samples were divided into three matched sets of 12 samples each.  Each individual sample was then weighed and the moisture content measured as described above.



Figure 3.1     Cutting of matched flatsawn samples lengthwise



Figure 3.2     Cutting of matched quartersawn samples lengthwise

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One set of the flatsawn decking samples were treated with a 3% resin acid waterborne solution using a full-cell process. The Pamite 90™ resin acid employed was a commercial by-product from pulping, tall oil rosin commonly known by the acronym TOR, provided by Eastman Chemical Company. The waterborne formulation was made using 0.95 equivalents relative to resin acid of sodium hydroxide (NaOH) and 6% isopropanol, as described earlier (Schultz et al. 2007a). The matched set of control samples was untreated. The three matched sets of quartersawn samples were treated by a full-cell process with either waterborne 3% TOR, 3% paraffin wax in toluene for the positive controls, or the untreated negative control samples untreated. As these samples were relatively short the samples were end-coated with a phenolic-resorcinol adhesive after air drying.

The samples were installed on exterior shingled roofs at Mississippi State University, with the roofs slanted south to maximize the sunlight and heat exposure, with the flatsawn samples all bark-side up (Figure 3.3). During the summer months the shade temperature will often rise to around 38°C, but on a sunny August day the roof temperature was measured at 72°C and the wooden samples 57°C using a Westward Infrared non contact thermometer. The flatsawn samples had been in this outdoor exposure for 22 months prior to the start of the experiment and the quartersawn samples 12 months to ensure that the water repellent system was durable. During the approximately 10 weeks that this exposure study was conducted, from the end of July to the beginning of September when the Mississippi temperatures are the highest, the samples were periodically weighed before predicted rain, right after and then one or two days later. One unusually heavy storm with 8 cm of rain over 12 hours occurred during

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this period as the remnants of a hurricane came through, but most storms were less then 1 hour with 1 to 3 cm of rain, with a few light sprinkles also occurring. The extent of checking was measured at the end of the experiment on the flatsawn samples using a scale of 0 to 4, where a "0" is no checking, "1" light checking, up to a "4" where the checking was so bad that the board could be bent by hand. The quartersawn samples were also inspected for checking, but as the splits often occurred in the laminated joint the extent of cupping was measured instead.



Figure 3.3    Roof test setup showing 32 mm x 140 mm decking board sections

## Results and Discussion

### Moisture Content Variation

The average moisture content over time of the flatsawn test boards during the study period is shown in Figure 3.4. Considerable variation in the MC change among individual untreated sapwood samples was observed. For example, for the last rain in

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this study the MC gain for the control boards ranged from a low of 22.3% to a high of 42.0%, with an average of 30.9%   The wide variability was to be expected based on prior studies on the inherent permeability and hydrophobic extractive variations in southern pine sapwood (Nicholas et al. 2005; Schultz et al. 2007a).  These large and rapid MC changes in the untreated decking lead to stresses and subsequent poor dimensional stability.  For example, starting at about 680 days of exposure three short-duration rains occurred over an eight-day period causing rapid increases in the MC of the untreated samples followed by rapid drying, which led to multiple and rapid swelling and shrinking cycles.   Interestingly, the average MC of the untreated decking following rain was not highly dependent on the amount of rain, with average MCs after rain ranging from approximately 30% to 40% after summer rains of 1 to 3 cm, and an average MC of only 41% measured after an unusual 8 cm of rain over 12 hours.  During a prolonged period of hot and dry weather the MC dropped to as low as 4%.

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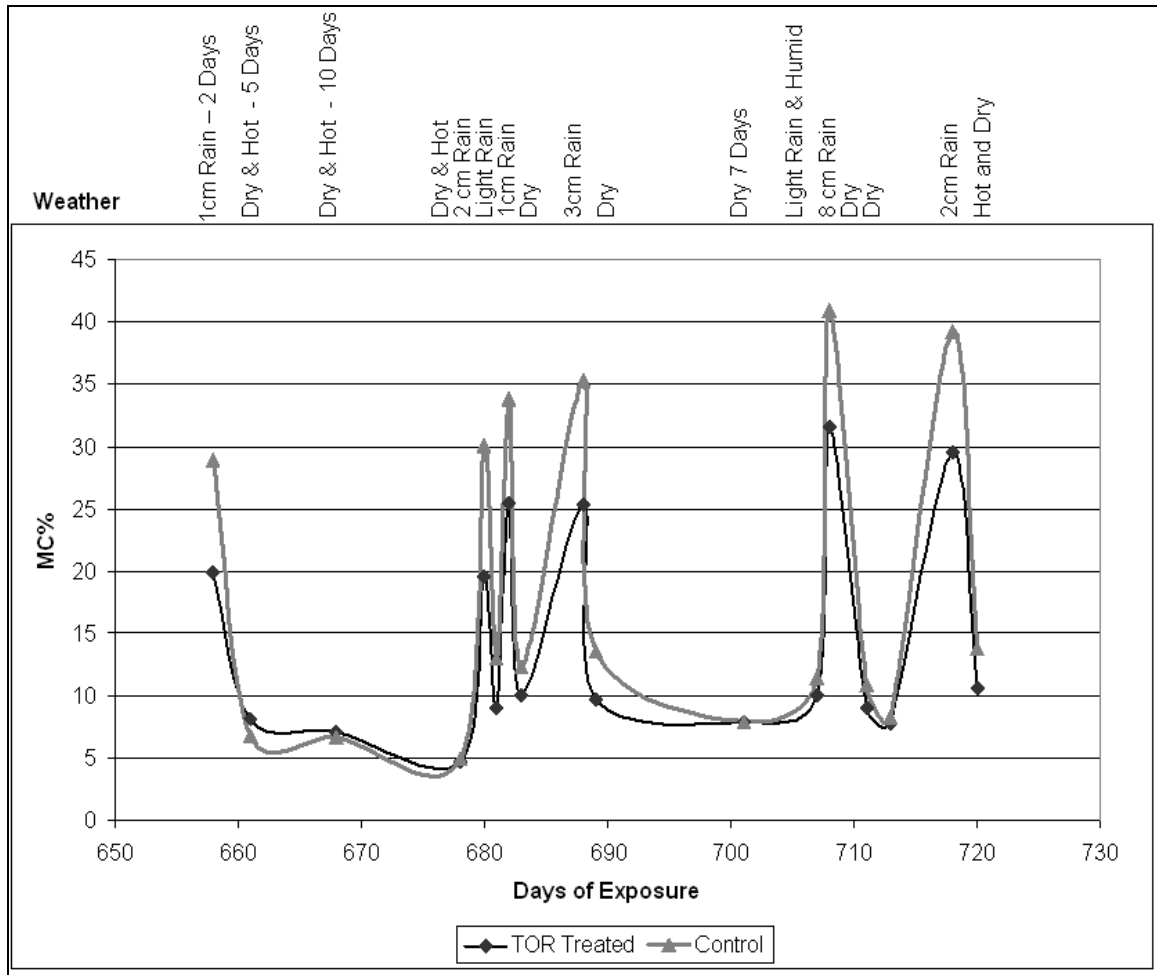
Figure 3.4    Average moisture content over the period of study for the matched
              flatsawn decking samples that were untreated or treated with 3% tall oil
              rosin (TOR) in response to the weather conditions that are indicated on the
              top of the graph

When comparing the average MC of the TOR- versus untreated samples, it can be

seen from Figure 3.3 that the treated boards gained less moisture following rain but then

dried to about the same MC as the untreated boards within only a few summer days.

Thus, the TOR treatment did impart some water repellency to the decking. For days 718

to 720, the average MC gain for the untreated flatsawn samples (26.1%) was significantly

different than the TOR samples using an analysis of variance test (18.9%) (p-value =

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0.0016).  Furthermore, because these samples had been in outdoor exposure for almost two years prior to the start of this study, it appears that the TOR treatment is effective over long periods.

The average MC of the quartersawn samples is shown in Figure 3.5, with a similar pattern as observed in Figure 3.4.  Both sets equilibrated to similarly low MC's with both treated and untreated samples; however, untreated and TOR-treated quartersawn samples attained a higher MC than the flatsawn samples after the same rain exposure. In comparing the MC of the untreated, TOR-treated, and wax-treated quartersawn boards, it is apparent that the paraffin wax provides extremely good water repellency, as expected.  The amount of wax employed in this study was much greater than that used in commercially-treated water-repellent decking.  While the TOR treatment was not as effective as the wax it did reduce the amount of moisture gained by rain by about one-third, as was also observed in the flatsawn decking.  For days 423 to 425, the average MC gain for the three treatments were significantly different using an analysis of variance test (p-value = <0.0001), with untreated quartersawn samples having an average MC gain of 33.4%, TOR samples 26.2%, and paraffin wax samples 5.2%.

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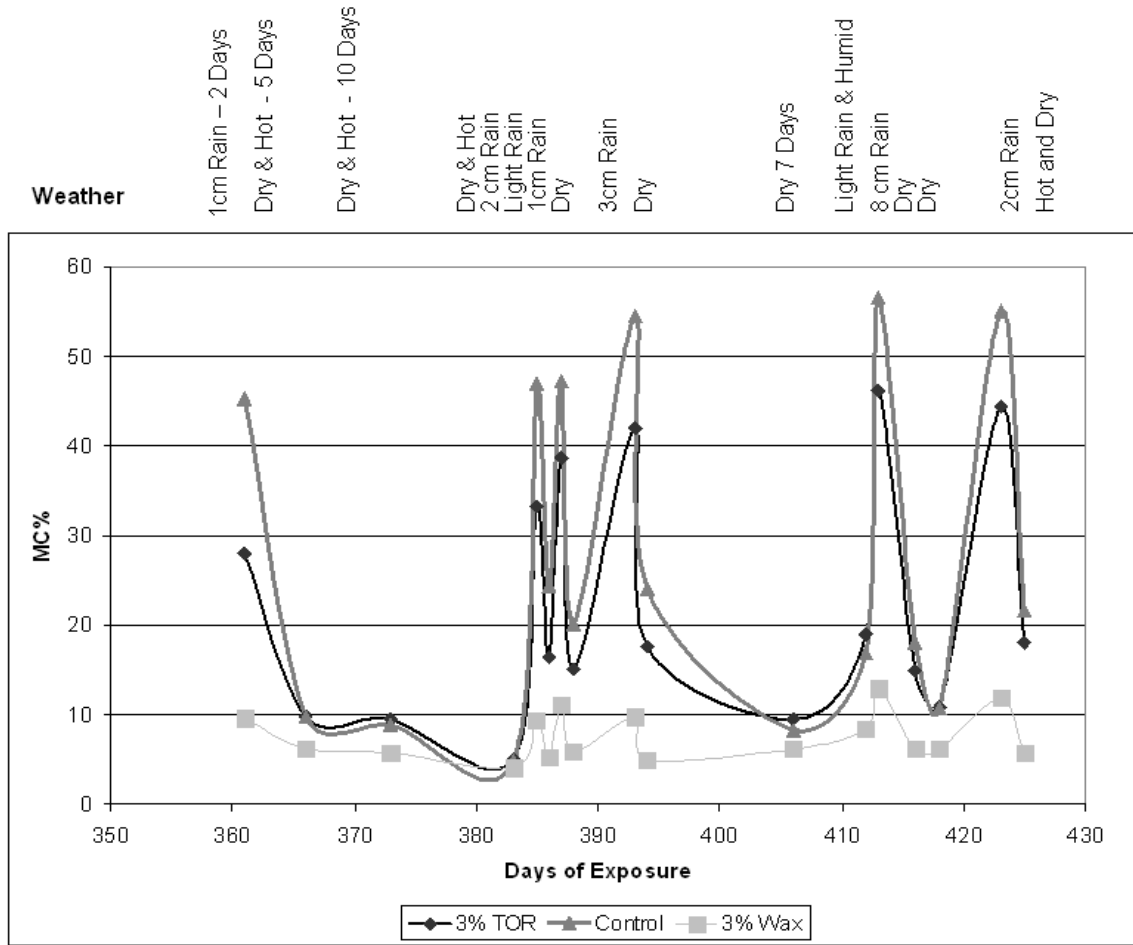
Figure 3.5    Average moisture content over the period of study for the matched
              quartersawn decking samples that were untreated, treated with 3% tall oil
              rosin (TOR), and treated with 3% wax in response to the weather
              conditions that are indicated on the top of the graph

## Dimensional Stability

As discussed above, the reduction in MC gained by the TOR-treated flatsawn

samples following rain was about one-third relative to the untreated controls.  The

average checking for the flatsawn control samples was 3.2, with one sample having a low

"1" while seven of the 12 controls had the severest "4" ranking.  This was significantly

greater using an analysis of variance test than the TOR-treated flatsawn samples that had

an average 2.1 ranking, which ranged from three "1's" (light checking) to four samples

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with moderately severe "3" rankings (p-value = 0.01).  A regression model was fitted for the two flatsawn treatments with MC gain as the independent variable and the average checking rating as the dependent variable.  For the untreated flatsawn samples, the change in MC explained 40% of the variability in the splitting rating ($R^2 = 0.4$).  For the TOR-treated samples, the change in moisture content explained 50% of the variability in the splitting rating ($R^2 = 0.5$). For the quartersawn treatments, the paraffin wax treatment had significantly less cupping (1.3 mm) than the untreated (4.2 mm) and TOR-treated (3.4 mm) samples (p-value = <0.0001).

Although not a study objective, five of the 12 control quartersawn samples had fungal decay at the end of the study.  The samples with decay all had higher MC's following rain than the average overall MC of the untreated boards.  The higher MC could be due to a lower level of hydrophobic extractives (resin acids, fatty acids, and monoterpenes) in the decayed untreated sapwood samples compared to the non-decayed controls (Schultz et al. 2005; Schultz et al. 2007a).  Furthermore, as resin acids are known metal complexing agents and, thus, would provide some decay resistance to wood, relatively low levels of resin acids may result in sapwood being more susceptible to decay (Schultz and Nicholas 2002; Schultz et al. 2007b; Dahlen et al. 2009).  We therefore suspect that the five samples with decay have relatively low inherent levels of resin acids.

Based on this study, it may be possible to employ renewable and economical resin acids to enhance the dimensional stability of lumber.  Furthermore, if naturally present resin acids are found to enhance the dimensional stability and decay resistance, it may be

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possible to genetically select trees to provide lumber with these desirable properties (Schultz et al. 2007c).

## Conclusions

Flatsawn and quartersawn southern pine sapwood decking samples treated with a low-cost waterborne resin acid system and exposed to a harsh above-ground environment for up to two years had enhanced water repellency compared to the untreated samples.  A wide variation in moisture gained after a rain was observed for the untreated flatsawn decking which was significantly and positively correlated to the extent of splitting. Although the amount of water gained was only reduced by about one-third for the TOR-treated boards compared to the untreated boards, this significantly lowered the splitting and cupping.  We are continuing these studies and plan to report in the near future on the possible enhanced fungal protection obtained by resin acids alone or combined with organic biocides.

## Literature Cited

Dahlen, J., T.P. Schultz, L. Prewitt, and D.D. Nicholas. 2009. Effect of chemical and physical properties on the decay susceptibility of southern pine sapwood decking in two aboveground exposures. Forest Products Journal 59(9):74-78.

Evans, P. 2003. Emerging technologies in wood protection. Forest Products Journal 53(11), 14-22.

Goodell, B. 2003. Brown-rot fungal degradation of wood: Our evolving view. In Wood Protection and Preservation: Advances in our Changing World; Goodell, B., Nicholas, D.D. and Schultz, T.P., eds. American Chemical Society Symposium Series 845, Washington, D.C. chp. 6.

Henry, W.P. 2003. Non-enzymatic iron, manganese and copper chemistry of potential importance in wood decay. In Wood Protection and Preservation: Advances in our Changing World; Goodell, B., Nicholas, D.D. and Schultz, T.P., eds. American Chemical Society Symposium Series 845, Washington, D.C. chp. 10.

Kabir, F.R.A., D.D. Nicholas, R.C. Vasishth, and H.M. Barnes. 1992. Laboratory methods to predict the weathering characteristics of wood. Holzforschung 46, 395-401.

Nicholas, D.D., T.P. Schultz, L. Sites, and D. Buckner. 2005. Effect of permeability and extractives on the decay rate of southern pine sapwood in above ground exposure. Internat. Research Group on Wood Protec. Paper 05-20310.

Preston, A.F. 2000. Wood preservation: Trends of today that will influence the industry tomorrow. Forest Products Journal 50(9), 12-19.

Preston, A.F. 2003. Can understanding the mechanisms of biodegradaton help preservative development? In Wood Protection and Preservation: Advances in our Changing World; Goodell, B., Nicholas, D.D. and Schultz, T.P., eds. American Chemical Society Symposium Series 845, Washington, D.C. chp. 22.

Rodriquez, J., A. Ferraz, and M.P. de Mello. 2003. Role of metals in wood biodegradation. In Wood Protection and Preservation: Advances in our Changing World; Goodell, B., Nicholas, D.D. and Schultz, T.P., eds. American Chemical Society Symposium Series 845, Washington, D.C. chp. 9.

Schultz, T.P., and D.D. Nicholas. 2002. Development of environmentally-benign wood preservatives based on the combination of organic biocides with antioxidants and metal chelators. Phytochemistry 61, 555-560.

Schultz, T.P., D.D. Nicholas, W.P. Henry, C.U. Pittman, W.O. Wipf, and B. Goodell. 2005. Review of laboratory and outdoor exposure efficacy results of organic biocide:antioxidant combination, and initial economic analysis and discussion of a proposed mechanism. Wood and Fiber Science 37, 175-184.

Schultz, T.P., D.D. Nicholas, and L.L. Ingram Jr. 2007a. Laboratory and outdoor water repellency and dimensional stability of southern pine sapwood treated with a waterborne water repellent made from resin acids. Holzforschung 61, 317-322.

Schultz, T.P., D.D. Nicholas, and S.S. Kelley. 2007b. Nonleachable water-borne wood preservation composition. Patent Appl. WO 2007-US64535, 2007.

Schultz, T.P., D.D. Nicholas, and A.F. Preston. 2007c. A brief review of the past, present and future of wood preservation. Pest Management Science 63, 784-788.

Vlosky, R.P., and T.F. Shupe. 2004. U.S. homebuilder perceptions about treated wood. Forest Products Journal 54(10), 41-48.

CHAPTER IV

# EFFECT OF CHEMICAL AND PHYSICAL PROPERTIES ON THE DECAY SUSCEPTIBILITY OF SOUTHERN PINE SAPWOOD DECKING IN TWO ABOVE-GROUND EXPOSURES

**Abstract**

Southern pine (*Pinus* spp.) sapwood has variable decay susceptibility. To study this variability, 23 flatsawn defect-free southern pine decking sapwood boards, 5/4 by 6 inch nominal, were obtained. Samples 39.4 cm long were cut from each board, immersed in water for 24 hours to measure initial permeability, then installed on a roof slanted towards the sun to ensure maximum drying rate and stress following rainstorms. Small samples from each board, 6.4 x 6.4 cm, were also installed in a ground proximity test designed to maximize moisture retention following rains and provide some additional moisture and nutrients through ground water wicking. Samples from each board were also analyzed for a variety of chemical and physical properties. The roof samples were frequently weighed before and after rain to determine estimated moisture content gain, and periodically rated for checking and decay. The ground proximity samples were also rated for decay. After two years of exposure the samples were cut into sections to better observe interior decay and rated for decay one final time.

The ground proximity samples (7.35 average decay rating) had only slightly more decay than the roof samples (7.85 average decay rating), despite the ground proximity

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samples having both a test arrangement and climate that encouraged fungal decay compared to the roof samples. The correlation between the final decay ratings for the matched samples in the two different environments was 37%, suggesting that above-ground decay susceptibility is dependent on the particular test methodology and macro- and micro-environment. Decay in roof exposure was best modeled using the initial moisture content gain/permeability, moisture uptake following rain, extent of checking, and the amount of dehydroabietic resin acid. Three, or all four, of these factors are related to the moisture content of wood, a critical factor in fungal decay. By contrast, the significant factors for decay in ground proximity, where the test arrangement encourages moisture retention, were the amounts of the hydrophobic extractives palmitic fatty acid and dehydroabietic and neoabietic resin acids.

## Introduction

A major use for treated lumber in North America is for outdoor decks, with most of this lumber cut from southern pines (SP). Being a natural organic material wood can be biodegraded, so in exterior exposure most wood products should be treated with a wood preservative to prevent fungal decay. When evaluating new potential wood preservatives for above-ground applications, high variability in the decay rates of replicate untreated sapwood control test samples has been observed (Nicholas et al. 2005); the decay difference results in an increased exposure time necessary to obtain definitive efficacy results for new preservative systems. The variation in decay susceptibility in SP sapwood could be due to physical properties such as density, and/or the presence of hydrophobic and/or hydrophilic extractives which exist in surprisingly

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erratic levels in green SP sapwood (Schultz et al. 2007b).  The role of hydrophilic and hydrophobic extractives on natural durability of sapwood in above ground exposure has received only limited study (e.g., Nicholas et al. 2005).  This preliminary study determined that the initial water permeability of SP sapwood significantly affected the decay rate.  Water repellency of SP sapwood, which would impact the sorption of water during rain, might affect the decay rate in above-ground exposure.  However, removal of the hydrophobic extractives by solvent extraction had a non-significant effect, perhaps due to opposing influence of the resin versus fatty acids.  Removal of the hydrophilic extractives significantly decreased the decay rate, perhaps by removing soluble sugars that would be a readily available food source for the bacteria and mold fungi that initially colonize wood (Nicholas and Crawford 2003).

Most studies on SP extractives have been conducted on green wood.  However, wood preservative and dimensional stability studies employ kiln dried lumber, where the high temperatures used to commercially dry SP lumber volatilize many of the monoterpenes and may chemically alter terpenoids and other extractives.  Further, during high temperature drying the hemicelluloses may be partially hydrolyzed to give easily digested simple sugars, and free water movement may reduce the wood permeability by entrapping hydrophobic extractives in the margos of aspirated pits.

For this study 23 SP sapwood decking boards were obtained, 32 x 140 mm, and the relative density, growth rate, chemical composition of the extractives (fatty and resin acids, nitrogen, and reducing sugar contents) were determined.  The initial water permeability was measured by soaking for 24 hours.  Samples were then installed in two different above-ground locations.  One location was on top of a roof slanted towards the

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sun in an area with relatively dry summers, so that any moisture gained during a summer rainstorm would be quickly evaporated, (Figure 3.3). The second environment was an AWPA E-18 (AWPA 2008) ground proximity test that is designed to minimize moisture loss, and placed in a location with relatively wet summers and mild winters (Figure 4.1). The ground proximity test would also provide some nutrients by water wicking up from the ground and nitrogen during rainfall, while the roof samples would obtain only minimal nutrients by airborne particles and nitrogen during rainfall (NADP 2010). Both sets were periodically inspected visually and rated for decay in accordance with AWPA E-18 standard (AWPA 2008). The roof samples were also rated for checking, and periodically weighed before and after rain to obtain moisture gain profiles. After two years of exposure the samples were sliced into four pieces to more easily see interior decay pockets and rated for decay a final time.

Figure 4.1    Ground decay test setup; samples are beneath the screen cover

The objectives of this study were to determine: 1) which factors are significantly correlated with decay for the sapwood samples in the two different above-ground test environments; and 2) how similar the decay extent is for the matched samples in the two different environments.

**Materials and Methods**

Lumber

Twenty three flatsawn defect-free SP (*Pinus* spp.) decking sapwood samples, kiln-dried, 32 x 140 mm, were obtained from an Alabama lumber mill.  Samples 39.4 cm in length were cut from each board and labeled with the original board code, and an adjacent small 2.5 cm long sample was also cut (Figure 4.2).  The small samples were

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then oven-dried to obtain an estimated moisture content and oven-dry weight for the 39.4 cm long samples. The relative density of each board was determined by the oven-dry weight, and the growth rate based on the number of annual rings per 2.5 cm in the radial dimension. The 39.4 cm samples were completely immersed in water for 24 hours to obtain permeability by weight gain and then installed in Starkville, MS, on a roof slanted towards the sun to ensure maximum drying rate and stress following rainstorms. Temperature measurements during an August noon showed roof shingle temperatures of $72^{o}$C and wood at $57^{o}$C. Starkville is in an AWPA deterioration hazard zone of 4, or high, with relatively dry summers (Schultz et al. 2002).
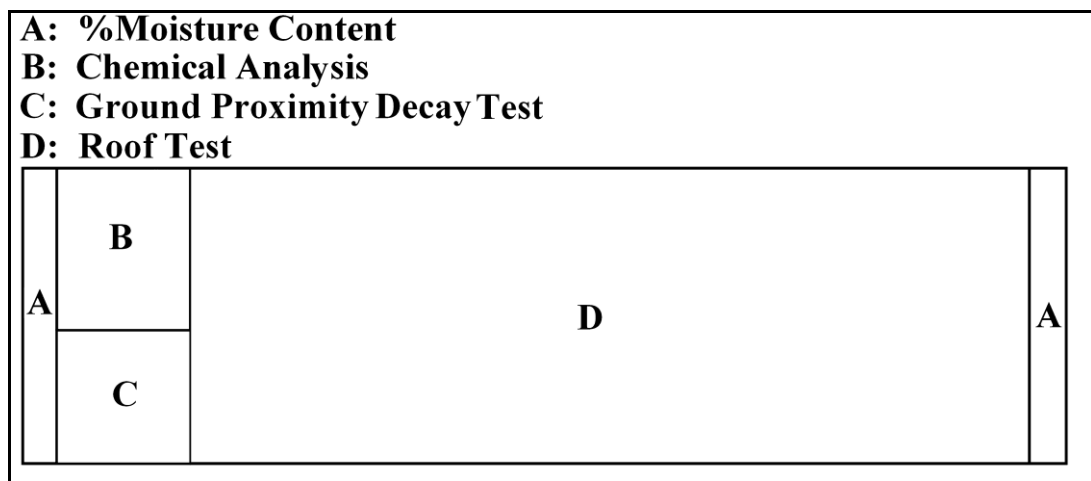


Figure 4.2    Board cut into samples

Small samples from each board, 6.4 x 6.4 cm, were also installed in an AWPA E-18 ground proximity test at the Saucier, MS, test plot, which consisted of concrete cinder blocks laid on top of the ground soil. The small wood samples were laid on top of the cinder blocks, with a shade cloth lid covering the top. The AWPA E-18 test is designed to maximize moisture retentions following rain, unlike the roof samples in Starkville.

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Water can also wick up from the soil in the ground proximity test, further keeping the boards wet and potentially providing some nutrients essential for decay.  Saucier Mississippi is in a severe, or 5 deterioration AWPA zone, with relatively mild winter temperatures and wet summers (Schultz et al. 2002).  Thus, both the test arrangement and local climate indicated a higher fungal decay hazard for the Saucier ground proximity compared to the Starkville roof samples.

The roof samples were periodically weighed before and after rain to determine the estimated moisture content gain during storms.  The boards were also periodically rated for checking and decay.  The checking of the boards was rated with a scale of zero to four, where a "0" was no checking and a "4" such severe checking that the board would fail structurally.  The fungal decay was rated based on the AWPA E-18 scale, with a "10" indicating no decay and "0" denoting total failure.

<u>Chemical Analysis</u>

Representative sections (Figure 3) from each board were ground in a Wiley mill to 10 mesh.   The nitrogen contents were analyzed using a micro-Kjeldahl method; all samples had less than 0.1% N so no values are reported.  The free sugar content was performed by the Somogyi-Nelson Alkaline Copper method (Marais et al. 1966), using glucose to develop the response curve.  The sugars were heated in a solution of copper tartrate; and reacted with arsenomolybdate to form molybdenum blue.  The solution was analyzed with a spectrophotometer at the 510 nm wavelength.  The resin and fatty acid analysis was performed by extraction of the wood then derivatization of the extract with N,O,-Bis(Trimethylsilyl)trifluoroacetamide (BSTFA)  to form methyl esters.  The

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methylated extractives were then analyzed on a GC/FID with an Agilent Ultra 2 (30 m x 0.2mm, 0.33 μm film) column, employing methylated standards and retention times to identify fatty and resin acids compounds and response curves for quantification.

### Statistical Analysis

The roof exposure decay and ground exposure decay response variables were separately analyzed with a multiple regression model in SAS.  A variable selection method was used to determine which variables were significant for each multiple regression model.  The explanatory variables used in the variable selection models were water absorbed when fully submersed for 24 hours (permeability), the average amount of water absorbed during rainstorms (rain absorption), the check rating, the mold rating, the amount of individual fatty and resin acids, the soluble sugar content, the oven dry weight (density) of the sample, and the rings per inch (growth rate).  The multiple regression model used was:

$$Y_i = B_0 + B_1 X_1 + B_2 X_2 ... + B_i X_i + \varepsilon_i \qquad (4.1)$$

Where $y_i$ is the ground or roof decay rating, $B_0$ is the intercept, $i$ is the number of response variables selected in each of the multiple regression models, $B_i$ is the slope of each response variable, $X_i$ is each response variable selected, and $\varepsilon_i$ is the error term. Higher decay ratings have less decay, so a decay rating of ten equals no decay.  A positive slope for a response variable equals a higher decay rating, or less decay, when the value of a response variable is relatively high, while a negative slope for a response variable equals a lower decay rating, or more decay, when the value of the response variable is relatively high.

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## Results and Discussion

The correlation between final decay ratings for the matched samples on the roof and ground proximity tests was only 37%. This suggests that above-ground decay susceptibility is dependent on the particular test and macro- and micro-environment where the wood resides. Surprisingly, the ground proximity samples (7.35 decay rating, 1.9 standard deviation) had only slightly more decay than the roof samples (7.85 decay rating, 2.5 standard deviation), despite the ground proximity samples having both a test arrangement and climate that encouraged fungal decay compared to the roof samples.

The significant variables for the decay model for the roof samples were permeability (positive), rain absorption (negative), check rating (positive), and amount of dehydroabietic acid (positive). These factors gave a model with an $r^2$ of 0.76 (p-value < 0.0001) (Figure 4.3). The multiple regression model was calculated as:

$$Roof = 7.2 + 0.21 * p - 0.36 * r\_a + 0.71 * c + 0.80 * d \qquad (4.2)$$

**Predicted vs Actual Roof Decay**
**$r^2 = 0.76$**
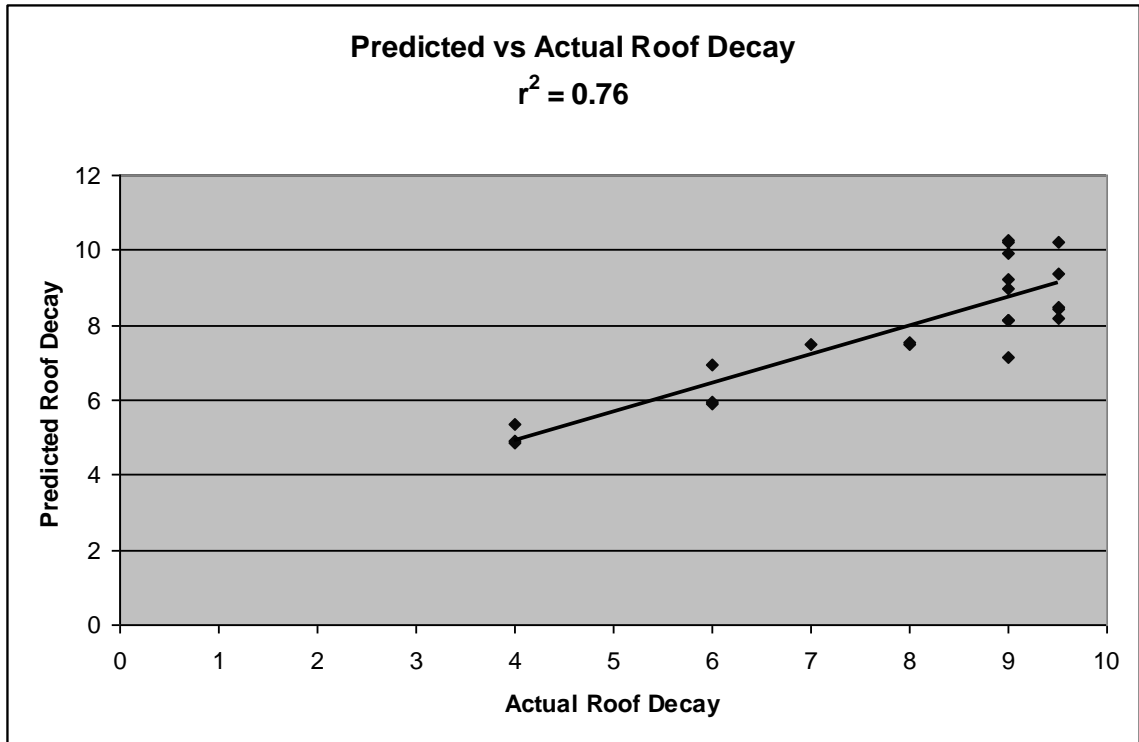
Figure 4.3    Predicted versus actual roof decay

The rain absorption is in agreement with a prior preliminary study (Nicholas et al. 2005) in that higher moisture is critical for decay (e.g., Nicholas and Crawford 2003), so more water absorption during rain results in greater decay. The permeability was also a significant factor but, surprisingly, positive, where more permeability modeled as less decay. However, when rain absorption and permeability were plotted, a positive linear curve with a good fit ($r^2 = 0.87$) was obtained; yet collinearity in the regression model was not a problem. This suggests that both variables affect the amount of moisture in wood after a rainstorm, but perhaps higher permeability results in both the board gaining more moisture during short summer rain storms but also drying out faster after the rain. Additionally, a third unknown factor may be compensated for by the model employing both permeability and rain absorption. The amount of checking influencing decay is

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likely also a factor in moisture. After a rainstorm more checking would increase the board's surface area so that it should dry faster, thus quickly reducing the moisture available for decay. The final significant factor, dehydroabietic acid (more resin acid equates to less decay), may be due to the resin acid acting as a water repellent (Schultz et al. 2007a, 2007b; Dahlen et al. 2008) and/or the resin acid complexing with the minimal metals present in wood that are employed by the decay fungi during biodegradation (Henry 2003; Schultz and Nicholas 2002; Binbuga et al. 2005). Specifically, we have found that adding metal complexing compounds to wood, including resin acids, reduce fungal decay (Schultz and Nicholas 2007, 2008). Thus, for the samples exposed on the roof where wood moisture can be quickly evaporated after rain it appears that three, or perhaps all four, of the significant factors are related to wood moisture.

The significant variables for the extent of decay for the AWPA E-18 ground proximity samples were palmitic fatty acid (negative), dehydroabietic resin acid (positive), and neoabietic resin acid (negative), with the model explaining 41% of the variation ($r^2 = 0.41$, p-value = 0.0155) (Figure 4.4). The multiple regression model was calculated as:

$$Ground = 8.9 - 4.62 * p + 3.76 * d + 0.71 * n \qquad (4.3)$$
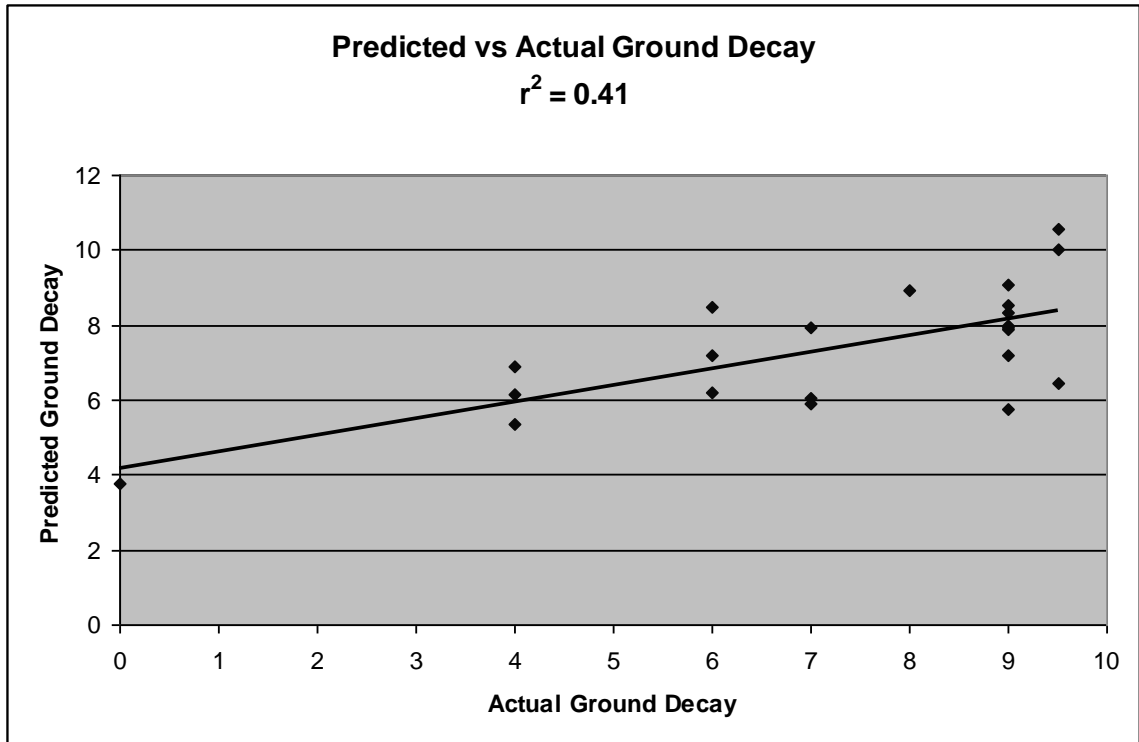
Figure 4.4    Predicted versus actual ground decay

Thus, in contrast to the roof samples where factors that increased moisture led to greater decay, the extent of decay in the ground proximity samples appeared dependent on the chemical extractives in the SP sapwood.  These differences would also explain the poor correlation in decay between the two sets discussed above.  Lesser palmitic fatty acid leading to reduced decay can be due to the fatty acid serving as a readily available food source for the bacteria and/or mold (Assarsson 1966; Martinez-Inigo et al. 1999; Dorado et al. 2000) that initially colonize wood.  Once the fatty acid is consumed these microorganisms could serve as a subsequent food source for decay fungi and, perhaps, also increase the nitrogen level in the wood (Nicholas and Crawford 2003) and so benefit decay fungi.  Conversely, dehydroabietic acid is relatively resistant to microbial attack but, as discussed above, can act as a water repellent and/or metal complexing agent to reduce fungal biodegradation.  Thus, greater levels of dehydroabietic acid leads to

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reduced decay. The negative effect of the neoabietic resin acid is a bit confusing. Perhaps an unknown factor that is correlated to neoabietic acid content is confounding the results. In both models the mold rating, soluble sugar content, oven dry weight (density) of the sample, and rings per inch (growth rate) did not explain any of the variability for either roof or ground decay.

## Conclusions

This study showed that the extent of decay for matched SP sapwood samples in two different above-ground exposures was dependent on the particular test methodology and environment. The significant factors for roof decay were permeability, rain absorption, check rating, and amount of dehydroabietic acid, while the significant factors for ground decay were palmitic fatty acid, dehydroabietic resin acid, and neoabietic resin acid. For samples placed on a roof facing the sun, where the moisture gained during short summer rains was quickly evaporated, it appeared that the significant factors explaining fungal decay were mainly or entirely related to the moisture content of the board. Conversely, for samples placed on a ground proximity test designed to minimize moisture evaporation and provide some moisture by water wicking up from wet soil, the significant factors for decay were the hydrophobic extractives. A hydrophobic fatty acid may have enhanced decay by serving as an available food source for microbes that initially colonize wood prior to decay fungi, while the hydrophobic dehydroabietic resin acid decreased the decay. Surprisingly, despite the optimal test methodology and environment for the ground proximity samples compared to the roof samples, the overall extent of decay for the former samples was only slightly greater than for the latter

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samples (7.35 compared to 7.85 decay rating), while the correlation between final decay

ratings for the matched samples on the roof and ground proximity tests was only 37%.

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## Literature Cited

American Wood Protection Association (AWPA). 2008. 2008 AWPA Book of Standards, AWPA, Birmingham, AL.

Assarsson, A. 1966. Wood resin, especially the change in chemical composition during seasoning of the wood. III. The chemical extraction of spruce wood resin during chip seasoning. Svensk Papperstidning 69(9):291-299.

Binbuga, N., K. Chambers, W.P. Henry, and T.P. Schultz. 2005. Metal chelation studies relevant to wood protection. 1. Complexation of propyl gallate with $Fe^{2+}$. Holzforschung 59:205-209.

Dahlen, J., D.D. Nicholas, and T.P. Schultz. 2008. Water repellency and dimensional stability of southern pine decking treated with waterborne resin acids. Journal of Wood Chemistry and Technology 28:47-54.

Dorado, J., F.W. Claassen, G. Lenon, T.A. van Beek, J.B.P.A. Wijnberg, and R. Sierra-Alvarex. 2000. Degradation and detoxification of softwood extractives by sapstain fungi. Bioresource Technnology 71:13-20.

Henry, W.P. 2003. Non-enzymatic iron, manganese, and copper chemistry of potential importance in wood decay. *In*: Wood Deterioration and Preservation: Advances in Our Changing World, B. Goodell, D.D. Nicholas and and T.P. Schultz, eds. American Chemical Society, Symposium Proceedings, Washington, D.C. Chapter 10.

Marais, J.P., J.L. de Wit, and G.V. Quicke. 1966. A critical examination of the Nelson-Somogyi method for the determination of reducing sugars. Analytical Biochemistry 15:373-381.

Martinez-Inigo, M.J., P. Immerzeel, A. Gutierrez, J. C.d. Rio, and R. Sierra-Alvarex. 1999. Biodegradability of extractives in sapwood and heartwood from Scots pine by sapstain and white rot fungi. Holzforschung 53:247-252.

National Atmospheric Deposition Program (NADP). 2010. Nitrogen in the nation's rain. http://nadp.sws.uiuc.edu/lib/brochures/nitrogen.pdf Accessed March 29, 2010.

Nicholas, D.D., and D. Crawford. 2003. Concepts in the development of new accelerated test methods for wood decay. *In*: Wood Deterioration and Preservation: Advances in Our Changing World, B. Goodell, D.D. Nicholas and and T.P. Schultz, eds. American Chemical Society, Symposium Proceedings, Washington, D.C. Chapter 16.

Nicholas, D.D., T.P. Schultz, L. Sites and D. Buckner. 2005. Effect of permeability and extractives on the decay rate of southern pine sapwood in above ground exposure. Internat. Research Group on Wood Preservation. Document No. IRG/WP/05-20310, IRG, Stockholm, Sweden.

Schultz, T.P., and D.D. Nicholas. 2002. Development of environmentally-benign wood preservatives based on the combination of organic biocides with antioxidants and metal chelators. Phytochemistry 61:555-560.

Schultz, T.P., D.D. Nicholas, and D.E. Pettry. 2002. Depletion of CCA-C from ground-contact wood: Results from two field sites with significantly different soils. Holzforschung 56:125-129.

Schultz, T.P., and D.D. Nicholas. 2007. Totally organic wood preservative systems for exterior residential applications. *In:* Wood Protection 2006, Barnes, ed., Forest Products Society, Madison, WI.

Schultz, T.P., D.D. Nicholas and J. Shi. 2007a. Water repellency and dimensional stability of wood treated with waterborne resin acids/TOR. Internat. Research Group on Wood Pres. Document No. IRG/WP/07-40364, IRG, Stockholm, Sweden.

Schultz, T.P., D.D. Nicholas and L.L. Ingram, Jr. 2007b. Laboratory and outdoor water repellency and dimensional stability of southern pine sapwood treated with a waterborne water repellent made from resin acids. Holzforschung 61:3176-322.

Schultz, T.P., and D.D. Nicholas. 2008. Improving the performance of organic biocides by using economical and benign additives. *In*: Development of Commercial Wood Preservatives: Efficacy, Environmental, and Health Issues. T.P. Schultz, H. Militz, M.H. Freeman, B. Goodell, and D.D. Nicholas, eds. American Chemical Society, Symposium Proceedings 982, Washington, D.C. Chapter 16.

# CHAPTER V

# VOLATILE ORGANIC COMPOUNDS EMITTED DURING THE KILN

# DRYING OF SOUTHERN PINE UTILITY POLES

**Abstract**

Southern pine is the most common species used for utility poles in the U.S. Information regarding air emissions from pole drying is however very limited. With respect to drying, poles have longer lengths which result in limited end grain exposure, higher final moisture content, lower surface area to volume ratios, and typically southern pine poles have higher amounts of heartwood compared to southern pine lumber because of pole age.  For this research, several green southern pine utility pole bolts were obtained and cut into matched kiln charges that contained sapwood only, mostly sapwood, mostly heartwood, and knotty material.  Eight charges were dried at 110°C dry bulb with a wet bulb temperature no greater than 82°C until the poles reached a moisture content of 30% at a depth 76 mm from the surface.  Volatile organic emissions from the kiln charges were measured using federal guidelines. The mean emission values from the all sapwood, mostly sapwood, mostly heartwood, and knotty wood kiln charges were 3.59, 3.52, 2.64, and 3.65 pounds of volatile organic emissions per thousand board feet, respectively. The emissions of the sapwood, mostly sapwood, and knotty charges were similar to clear lumber emission values.  The emissions from the knotty charges were less than emissions from knotty lumber.  The results suggest that heartwood-rich utility poles

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release much less organic emissions than heartwood lumber, perhaps due to the band of sapwood which always surrounds the heartwood in poles whereas in lumber the heartwood is often exposed at the surface.

## Introduction

Southern pine (SP) is the species most commonly used in the production of utility poles (Micklewright 1992). To comply with local, state and federal laws, mills are required to obtain operating permits based on their estimated level of VOC emissions. Southern pine lumber typically averages between 3 and 4 pounds of VOCs emitted per 1,000 board feet (lb VOC/MBF) during kiln drying (Milota 2000).

In the absence of published data on drying poles, species specific emissions factors for lumber have been applied to pole kilns. However, with respect to drying, poles have numerous factors that differ from lumber. These include longer lengths which result in limited end grain exposure and thus slower drying times, higher final moisture content (MC), different schedules and lower surface area to volume ratios. Southern pine poles also have higher amounts of heartwood compared to lumber because lumber is increasingly harvested from relatively young small diameter southern pine trees that typically lack heartwood. Given the numerous differences between lumber and utility poles, the accuracy of using lumber emission factors for pole drying is somewhat questionable.

The objective of the study was to determine the volatile organic compound emissions from poles and to compare these results to previously published values of lumber to determine if applying emission factors to poles from lumber is reasonable. To

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address these issues charges of SP pole sections, as required in the Federal Register, were dried and the results are reported herein (Federal 2006).

## Materials and Methods

### Drying Procedure

Southern pine bolts were obtained from a local pole supplier. Sections were taken from the conveyor outfeed from the cutoff saw that followed the peeler. As such, the bolts were fresh. Each pole section was approximately 1829 mm long and 152 to 305 mm in diameter at the small end. The pole sections were selected based upon pole quality such that some poles contained only sapwood, some poles contained mostly sapwood but some heartwood, some poles would contain mostly heartwood, and some poles contained an abundance of knots. The knotty poles contained mostly sapwood material. Heartwood was detected visually. The mostly sapwood charges and knotty charges contained approximately 20% heartwood, while the mostly heartwood charges contained more than 50% heartwood. After transport to Mississippi State University, the pole sections were stored in a cooler at 2°C until drying. Two drying runs of each matched kiln charge were dried for a total of eight runs.

To first prepare the kiln test material, approximately 305 mm of length was removed from each end of each 1829 mm long bolt to eliminate any end drying that occurred during storage and handling. Approximately two 25 mm long discs were then crosscut to determine initial moisture content. One disc was weighed and oven dried to determine overall moisture content while the second disc was cut into three bands, core, material 76 mm from surface, and face material from each disc. Next, a single 584 mm

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long piece was cut from each of the pole sections and classified as sapwood, mostly sapwood, mostly heartwood, or knotty. As such, each kiln charge contained two or three pieces, each 584-mm long.  The poles from each kiln charge were measured prior to drying to determine green volume (cubic feet) and converted to board feet (1 cubic foot = 12 board feet) to facilitate comparison to VOC emissions from lumber values.

Poles are longer in length and have limited end grain exposure compared to lumber.  While lumber is commonly 8 to 16 feet in length, poles are commonly between 30 and 40 feet in length (Taylor 1996).  To prevent end drying in the kiln, urethane adhesive with aluminum foil was used as an end coating treatment on the transverse faces of the 584 mm sections (Figure 5.1). Urethane adhesive was selected because it adheres to green wood and aluminum foil and should not interfere with the VOCs analysis.  To ensure that the urethane adhesive was not adding to the emissions profile or deteriorating under the high temperature in the kiln, the urethane adhesive was tested separately after curing approximately two ounces of adhesive on a metal plate.  The adhesive was heated to 110°C in the pilot-scale kiln and tested for VOC emissions; no emissions were detected and the adhesive remained functional.  A previous study on emissions on SP lumber determined that end effect did not significantly affect VOC emissions (Shmulsky 2000).  Thus the end coating should only allow for the pole section in the pilot-scale kiln to more closely follow the drying of a commercial pole operation.  Once the ends of the pole pieces were sealed, the pieces were allowed to stand outside the kiln for approximately 24 hours in order to bring their temperatures to ambient and to allow for the resin to fully cure.

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Figure 5.1    Pole samples with urethane adhesive and aluminum foil

The pilot scale kiln is shown in figure 5.2.  The kiln schedule followed that of a commercial pole manufacturing facility. In general this kiln schedule required four hours of ramping to a dry bulb temperature of 110°C. The wet bulb temperature was no greater than 82°C, as required by pole drying standards when using a 110°C high temperature schedule (ANSI 1997).  The wet bulb depression was controlled with a mass flow controller via venting action with the quantity of air entering and thus leaving the kiln. Air velocity across the poles was approximately 213 meters per minute. The target drying time was 54 hours, as per the mill's schedule. Because the pilot-scale kiln often dries slightly faster than a commercial kiln, total drying time was dependent upon the individual charge necessary to arrive at the target final moisture content.  Poles are

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typically dried to 25% to 35% MC at a depth of 76 mm from the surface, depending on

the subsequent preservative treatment used (Boone 1994).  For this study, the poles were

dried to at least 30% MC 76 mm from the surface.  For each pole section, the final target

weight was estimated based on the moisture content of the two 25 mm sections cut and

dried from each pole.  Following drying, the moisture content of the poles was checked

by cutting a 25 mm disc from the center of the pole and subsequently cutting and drying

three bands, core, material 76 mm from surface, and face material from each disc to

verify proper drying.
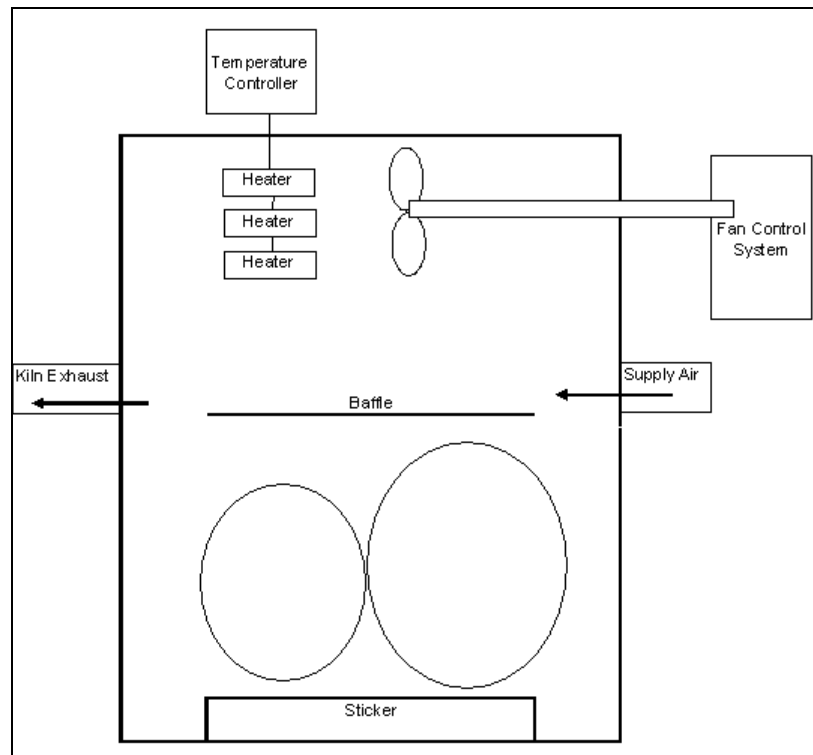


Figure 5.2      Pilot-scale kiln schematic

### Air Sampling for Total VOCs

Emissions sampling was performed according to 40 CFR 60 Appendix A Method

25A, through the use of a direct read flame ionization detection (FID) analyzer (EPA

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2006), and the National Council for Air and Stream Improvement (NCASI) Standard Protocol for VOC Concentration Measurement Method for Use at Small-Scale Kilns (Figure 5.3) (NCASI 1998).  A J.U.M. VE-7 instrument was used to determine the total hydrocarbons in the air exhaust of the kiln.  Based on a dry bulb temperature of 110°C and a wet bulb temperature of 82°C, the maximum gas moisture content in the kiln was calculated as 50%.  Because this is higher than the 20% gas moisture content recommended for the VE-7, the sample air was diluted with clean, dry compressed air. The compressed air was heated to approximately 121°C prior to dilution.
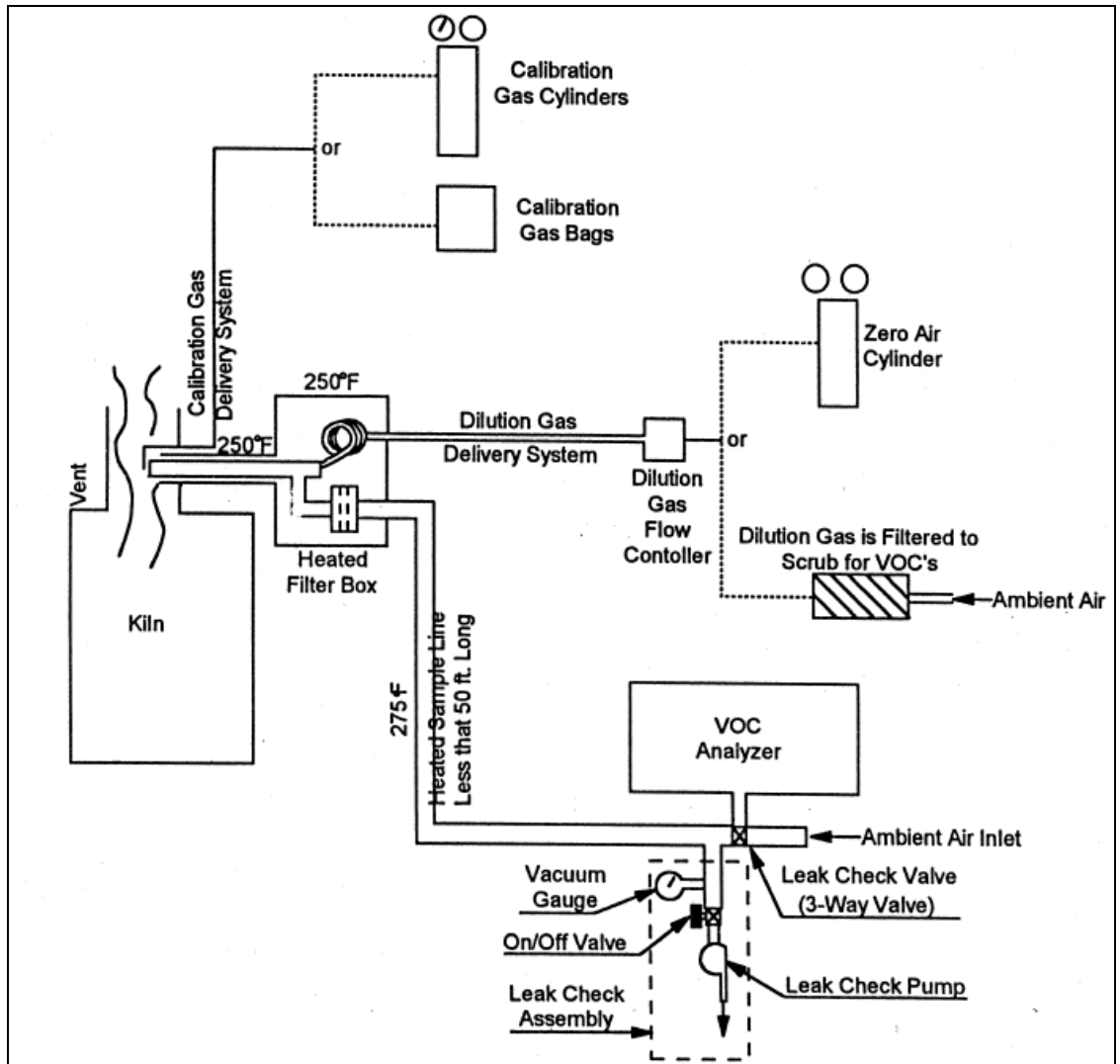
Figure 5.3    VOC sampling train (NCASI 1998)

Air sampling occurred continuously throughout the drying cycle. Calibration of the
J.U.M. VE-7 was performed at approximately 3-hour intervals.  As the FID results were
downloaded to a data-logger in "real-time," data gaps, for instance during calibration or
charge weighing, were encountered.  Effort was made to minimize these gaps and assure
that they did not exceed 45% of the total drying cycle time as per method criteria.  A
short description of the sampling protocol follows:

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1) Warm up total hydrocarbon analyzer (THC); 2) Vacuum leak check; 3) Calibrate (zero and span); 4) Calibration check (zero, span, mid); 5) Total flow check; 6) Turn on dilution system; 7) Sample flow check; 8) Sample check (span, mid); 9) Sample run; 10) Sample flow check; 11) Sample drift check (span, mid); 12) Turn off dilution system; 13) Total flow check; 14) Total drift check (span, mid, zero); 15) Final leak check

Steps 1 and 2 were performed only at the start of the drying cycle. Steps 3 through 7 were performed as part of each drying run (3 hour block). Step 15 was performed only at the end of the total drying cycle. To calibrate the total hydrocarbon analyzer, ultra high purity zero air was used and mid and span calibration gases were approximately 1000 and 3000 parts per million volume (ppmv) of propane in air, respectively. Each 3 hour time block was termed a sample run. At the end of the total drying time, the individual sample runs were assembled chronologically. Emissions data along with wood, moisture, and kiln information were assembled in order to calculate total VOC emissions. To this end, total VOC emissions as carbon per every thirty seconds were first calculated as per the NCASI method, which includes: instrument response, dry bulb temperature, wet bulb temperature, total flow rate, sample flow rate, atmospheric pressure, and gas moisture content of exhaust stack air. Then, the individual values from each thirty-second sampling event were summed to produce the total VOC emissions. Detailed instructions are found in NCASI (NCASI 1998).

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## Results and Discussion

Average moisture content of the charges for the sapwood, mostly sapwood, mostly heartwood, and knotty charges was 83%, 80%, 41%, and 82%, respectively. Average volume of the charges for the sapwood, mostly sapwood, mostly heartwood, and knotty charges was 0.041, 0.043, 0.071, and 0.065 cubic meters, respectively.

The maximum ppmv values during all of the charges did not exceed the span calibration gas and the VE-7 drift did not exceed the allowable tolerances and cause data loss. All leak checks were passed. A graph of the total hydrocarbon release from a sapwood charge is shown Figure 5.4.
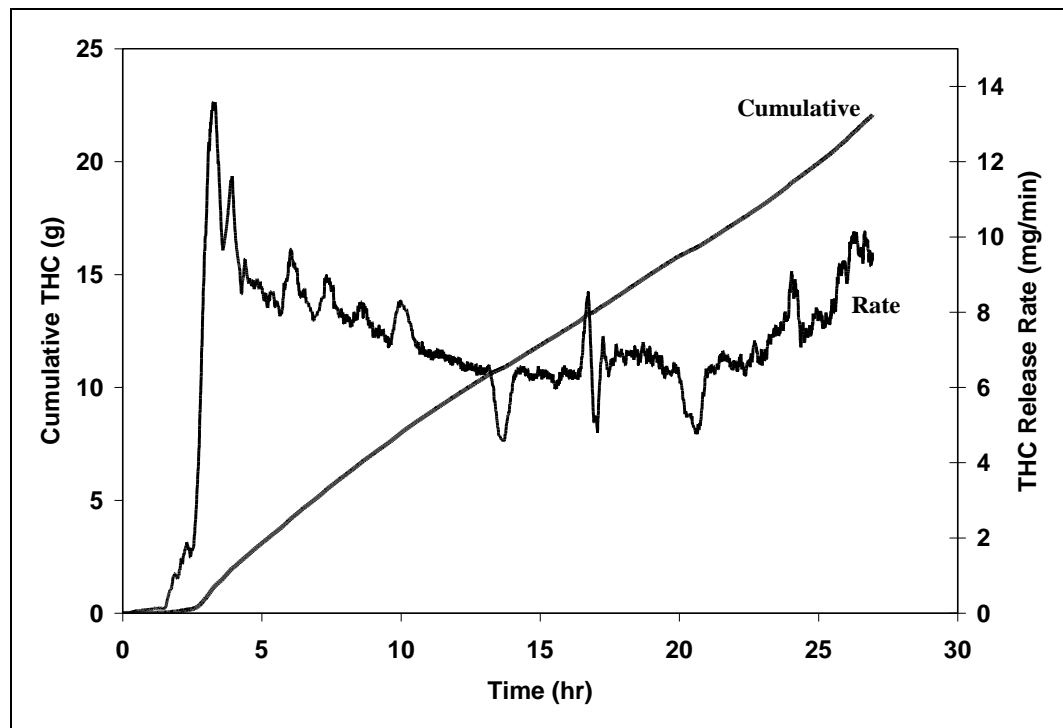


Figure 5.4      Emissions release for sapwood run #1

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Table 5.1 lists the average VOC emissions as carbon for the different kiln charges and VOC emission data from previous studies on southern pine lumber dried to below 19% MC.  The sapwood, mostly sapwood, and knotty charges had similar emissions to previous results for clear southern pine lumber.  The knotty charges emitted less volatile organics than a previous study from knotty lumber.  Perhaps seasonal influence contributed to this difference, as seasonal influence has been shown to influence VOC emissions (Conners et al. 2001); or perhaps a combination of factors including season influence, knot size and quantity, heartwood amount, and the lower moisture content that poles were dried to influenced this.

Table 5.1     VOCs emitted during SP pole drying

| Charge | lb VOC / MBF | kg VOC / m$^3$ wood |
|---|---|---|
| Sapwood Poles | 3.59 | 0.79 |
| Mostly Sapwood Poles | 3.52 | 0.68 |
| Heartwood Poles | 2.64 | 0.52 |
| Knotty Mostly Sapwood Poles | 3.65 | 0.68 |
| SP (Milota 2006) | 3 to 4 | 0.72 to 0.96* |
| SP Sapwood (Ingram et al 2000) | 3.83 | 0.92* |
| SP Heartwood (Ingram et al 2000) | 11.16 | 2.68* |
| SP Knotty (Ingram et al 2000) | 5.46 | 1.31* |

\* kg VOC / m$^3$ wood calculated based upon lb VOC/MBF * 0.24 (Milota 2006)

The major difference found between emissions from poles and previous studies was with regard to heartwood emissions, 2.64 lbs per thousand versus 11.16 lbs in heartwood lumber (Ingram et al. 2000).  Perhaps the difference is due to the band of sapwood which always surrounds the heartwood in poles.  This sapwood band potentially prevented organic material in the heartwood from migrating to the surface of the lumber

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and being released into the air.  In comparison, heartwood in lumber is often exposed at the surface and the organic compounds are easily volatilized.

With regard to volatile emissions and based on the results obtained in this study, it is reasonable to permit SP pole drying kilns using values obtained from clear SP lumber, regardless of the mixture of sapwood, heartwood, and knots in poles.

## Conclusions

Overall southern pine poles that were dried in this study had VOC emissions that were similar or less than previous studies based on the individual wood characteristics. The largest difference occurred with the mostly heartwood poles which had approximately a quarter of the VOC emissions than heartwood lumber had.  This was likely caused by the band of sapwood which always surrounds the heartwood in poles; this sapwood band likely prevented the terpenes from migrating to the surface of the wood and being released into the kiln air.  In contrast, the heartwood in lumber is often exposed at the surface and thus the terpenes are easily volatilized.  Many questions remain following this study such as how accurately do pole emissions from pilot-scale kilns emulate actual kilns, as well as what amounts of hazardous air pollutants are released from poles.

## Literature Cited

American National Standards Institute (ANSI).  1997.  Specifications and Dimensions for Wood Poles.  ANSI, New York.

Boone, R.S.  1994.  Drying of Southern Pine Poles for Preservative Treatment. Proceedings of the 1st southeastern pole conference.  Forest Products Society:  157-162.

Conners, T.E., L.L. Ingram, W. Su, H. Yan, S. Banerjee, A.T. Dalton, M.C. Templeton, and S.V. Diehl.  2001.  Seasonal Variation of Southern Pine Terpenes.  Forest Products Journal 51(6): 89-94.

Environmental Protection Agency (EPA). 2006. Method 25A – Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer. United States Environmental Protection Agency.  Washington, DC.

Federal Register. 2006. 71(32):8387. Appendix C to Subpart DDDD of Part 63- Considerations for a Small-Scale Kiln Emission Testing Program. Thursday February 16, 2006, Rules and Regulations.

Ingram, L.L. Jr, R. Shmulsky, A.T. Dalton, F.W. Taylor, and M.C. Templeton.  2000. The Measurement of Volatile Organic Emissions from Drying Southern Pine Lumber in a Laboratory-Scale Kiln.  Forest Products Journal. 50(4):91-94.

Micklewright, J.T.  1992.  Wood preservation statistics, 1990:  A report to the wood-preserving industry in the United States.  American Wood-Preservers' Association, Woodstock, MD.

Milota, M.R.  2000.  Emissions From Wood Drying:  The Science And The Issues. Forest Products Journal  50(6):10 – 20.

Milota, M.R. 2006.  Hazardous air pollutant emissions from lumber drying.  Forest Products Journal 56(7/8): 79 – 84.

National Council for Air and Stream Improvement (NCASI). 1998 (estimated). Standard Protocol for VOC Concentration Measurement Method for Use at Small-Scale Kilns. Gainesville, Florida.

Shmulsky, R.  2000.  End-Grain Influence On VOC Emissions From Kiln-Drying Loblolly Pine.  Forest Products Journal.  50(5):21 – 23.

Taylor, F.W.  1996.  Kiln drying of southern pine poles.  Proceedings of the 2nd southeastern pole conference.  Forest Products Society:  35-38

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CHAPTER VI

# HAZARDOUS AIR POLLUTANTS AND VOLATILE ORGANIC COMPOUNDS EMITTED DURING KILN DRYING OF SOUTHERN PINE LUMBER DRIED TO INTERIOR AND EXPORT MOISTURE SPECIFICATIONS

**Abstract**

Emission of hazardous air pollutants (HAPs) from wood kilns are required by mills to comply with the Clean Air Act. If a mill emits 10 tons of a single HAP or 25 tons of total HAPs a mill is subject to the maximum achievable control technology ruling. Softwood lumber, including southern pine, is considered kiln dry when the wood moisture content reaches below 19%, but it is sometimes dried to 8% moisture content for export or for interior products. To study HAP emissions when drying to 8% moisture content, green lumber was obtained from a local mill and twelve charges were kiln dried using three schedules; a 99°C elevated schedule and a 116°C and 127°C high temperature schedule. The time required to dry to both 19% and 8% moisture content was recorded. A sample of the kiln exhaust was collected and analyzed for the HAP compounds methanol, formaldehyde, acetaldehyde, acrolein, and propionaldehyde using an EPA approved method developed by NCASI. For all three kiln schedules, when drying to below both 19% and 8% moisture content, methanol emissions would reach 10 tons per year before reaching 25 tons from total HAPs. The high temperature schedules had significantly greater HAP emissions than the elevated schedule. When drying from 19% to 8% moisture content, methanol and formaldehyde emissions increased by an average

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of 48% and 52%, respectively; thus not over drying is critical for reduced emissions. Volatile organic compounds were quantified using a direct read flame ionization detector and reported according to the NCASI VOC and EPA OTM-26 methods. Overall volatile emissions were similar to previous studies.

## Introduction

Softwood lumber, including southern pine (SP) (*Pinus spp.)*, is considered kiln dry when the moisture content (MC) of the wood reaches below 19%. As such, emission studies conducted to date on SP have focused on drying from green to between 15% and 19% MC (Ingram et al. 2000; Milota 2006). The Forest Products Department at Mississippi State University has received inquiries into the additional release of hazardous air pollutants (HAPs) and volatile organic compounds (VOCs) when drying SP to 8% MC. Lumber dried to this lower MC is typically exported or used in interior applications such as millwork and flooring. Lumber that has been over dried can also frequently reach 8% MC.

The amount of emissions released during kiln drying is important because lumber kilns are subject to the Environmental Protection Agency's (EPA) Plywood and Composite Wood Product National Emissions Standards for Hazardous Air Pollutants (PCWP NESHAP) ruling (Federal 2006) that was finalized in 2006 and subsequently through the court system in 2007 (Federal 2007). Under this ruling, a facility is considered a major source of HAPs when more than 10 tons of a single HAP or 25 tons of total HAPs are emitted per year. Major sources of HAPs must install the maximum achievable control technology (MACT) available to reduce their emissions. The ruling

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lists six chemicals: methanol, formaldehyde, acetaldehyde, acrolein, propionaldehyde, and phenol into "total HAPs" for the PCWP NESHAP ruling (Figure 6.1) (Federal 2006). These six compounds represent approximately 96% of the HAPs associated with plywood and oriented strand board mills (Federal 2006). In addition to the total HAPs associated with drying, there are numerous organic compounds in the exhaust of kilns that are water soluble. Common volatile compounds and their respective molecular formula and boiling points are shown in Table 6.1.
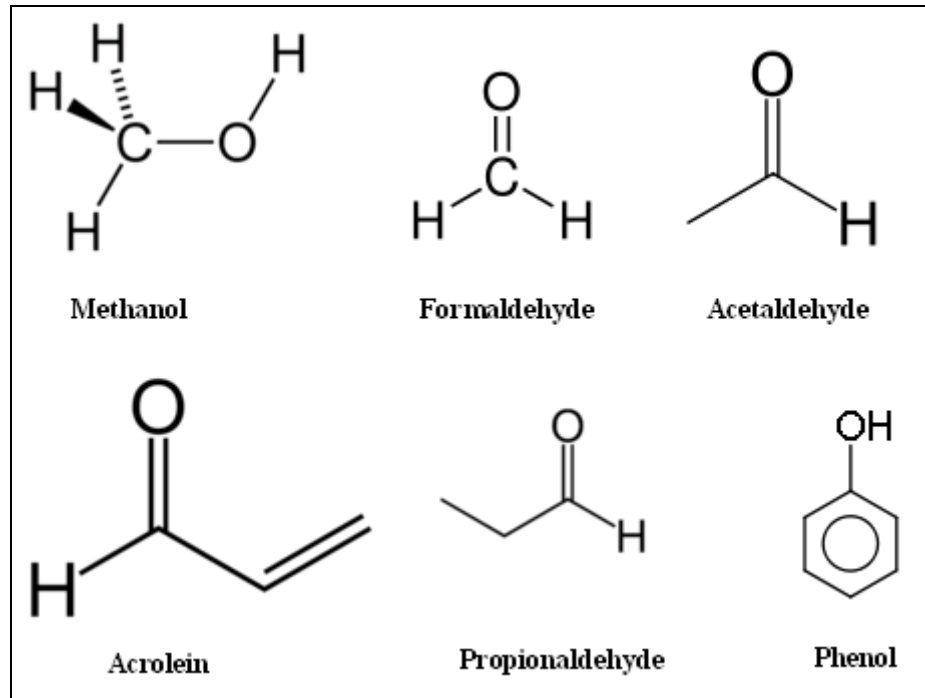


Figure 6.1    HAPs associated with the wood drying and composite industry

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Table 6.1    Common volatile chemicals emitted during SP kiln drying

| Chemical | Formula | Boiling Point |
|---|---|---|
| Water | $H_2O$ | 100°C |
| Formaldehyde | $CH_2O$ | -21°C |
| Methanol | $CH_4O$ | 64.7°C |
| Acetaldehyde | $C_2H_4O$ | 20.2°C |
| Ethanol | $C_2H_5OH$ | 78.4°C |
| Acrolein | $C_3H_4O$ | 53°C |
| Propionaldehyde | $C_3H_6O$ | 46°C |
| Acetone | $C_3H_6O$ | 56.5°C |
| 2-Propanol | $C_3H_8O$ | 82.5°C |
| Methyl Ethyl Ketone | $C_4H_8O$ | 79.6°C |

The associated health effects of these HAPs include irritation of the throat, eyes, nose, and skin (ATSDR 1990; Calabrese and Kenyon 1991; HSS 1993). Formaldehyde and acetaldehyde are suspected human carcinogens (HSS 2005). Formaldehyde has been linked to tumors of the epithelium cells in lab animals (HSS 2005). Acetaldehyde has been linked to respiratory tract tumors in lab animals (HSS 2005). Methanol can cause blindness and propionaldehyde can cause liver damage (HSS 1993). Exposure to acrolein at 2 parts per million (ppm) is immediately dangerous to health and at 10 ppm can result in death (ATSDR 1990).

While lumber kilns are regulated under the current MACT ruling, they are currently not subject to emission controls; however, the EPA is considering an updated ruling which may require control technology for lumber kilns (Law 2009). In the future, if lumber kilns are subject to control technology, major sources of HAPs would be required to install equipment such that emissions are reduced by 90%. Also it is important to consider that emissions from all sources in a mill are used when determining total HAPs. If a mill is a major source of HAPs from its dry kiln the mill will need to

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comply with the boiler MACT (Milota 2005).  The HAP emissions from kilns are also important when a lumber mill is co-located with a plywood facility; the kiln and plywood HAPs could be such that the plywood press would be subject to the MACT controls.

The amount of VOCs released during drying is not an indicator of HAP emissions (Milota 2006) because HAPs are associated with thermal degradation of wood (Otwell et al. 2000).  As the wood MC decreases below 10% during drying the surface temperature of lumber increases because of the decreased evaporative cooling which results in an increase in HAP emissions (Su et al. 1999).  Lignin has a higher potential for releasing formaldehyde than cellulose or hemicelluloses while some extractives release formaldehyde while others act as scavengers (Schafer and Roffael 2000).  Generally, higher temperatures result in greater amounts of methanol and formaldehyde being released (Milota and Mosher 2006).  Methanol and formaldehyde emissions increase at higher rates and are at their highest concentrations during the final stages of drying compared to the other aldehydes when the lumber temperature is highest (Otwell et al. 2000; McDonald et al. 2004)

NCASI has developed three standardized methods to measure HAPs specifically for the lumber and composite industry (NCASI 2010).  Methanol, formaldehyde and phenol are collected and quantified with the 98.01 method which draws a sample of the kiln exhaust through a series of chilled impingers filled with water.  Methanol and phenol are quantified via a gas chromatograph (GC) with a flame ionization detector (FID) and formaldehyde is quantified colorimetrically.  The other aldehydes are not as stable in water and have lower than optimal recovery rates, particularly acrolein.  The NCASI 99.02 method was developed to capture the aldehydes that break free from the water and

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is also used to measure non-water soluble compounds such as terpenes. The method adds

an evacuated canister downstream of the sampling pump which is analyzed via a GC with

mass spectrometry (MS) and a preconcentrator. The method is complex and expensive

and because of that NCASI developed the 105.01 method which has a sample of the kiln

air drawn through a series of chilled impingers containing water and o-

benzylhydroxylamine (BHA). The methanol and phenol are absorbed in the water and

analyzed on a GC/FID while the aldehydes are derivatized by BHA to form aldehyde

oximes that are analyzed on a GC with a nitrogen phosphorus detector. Formaldehyde,

acetaldehyde, and propionaldehyde can also be quantified with the EPA TO 11 method

where aldehydes are derivatized on dinitrophenylhydrazine DNPH and analyzed via high

performance liquid chromatography (HPLC) or ultra performance liquid chromatography

(UPLC) systems; however the method is not valid for acrolein and acetone can cause

interference with formaldehyde analysis (EPA 1996).

A table of HAPs released from SP dried to below 19% MC is shown in Table 6.2.

The Federal Register lists acetaldehyde, acrolein, formaldehyde, and phenol emission

values of 0.065, 0.009, 0.034, and 0.01 pounds per thousand board feet of lumber dried,

respectively (Federal 2006). In contrast to the federal register, phenol is not released

during the kiln drying of lumber (Milota and Mosher 2008a). Based on past research a SP

mill drying to 19% MC will reach 10 tons of methanol before reaching 25 tons of total

HAPs. At conventional temperatures (82°C) acetaldehyde can exceed methanol

emissions from wood species other than SP (Milota and Mosher 2008b).

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Table 6.2    Previous studies of HAPs emitted during SP lumber drying (lb chemical/MBF)

| Source | Species | Temperature | Methanol | Formaldehyde | Acetaldehyde | Acrolein | Propionaldehyde |
|---|---|---|---|---|---|---|---|
| NCASI 2002 | Loblolly pine | 113°C | 0.24 | 0.018 | 0.044 | 0.006 | 0.002 |
| NCASI 2002 | Loblolly pine | 113°C | 0.200 | 0.013 | | | |
| Milota 2006 | SP | 113°C | 0.107 | 0.0028 | | | |
| Shmulsky & Dahlen 2008 | SP | 116°C | | .0155 | .044 | .00815 | |
| Shmulsky & Dahlen 2008 | SP | 127°C | | .0135 | .0385 | .00565 | |
| Federal 2006 | | | | 0.034 | 0.065 | 0.009 | |

In 2007 the EPA released method OTM-26: Interim VOC measurement protocol for the wood products industry (EPA 2007). The method requires VOC permitting for wood products facilities based on total VOCs reported as propane and individual measurements of methanol and formaldehyde. The method allows for exempt VOC that have negligible photochemical importance to be subtracted from total VOCs; these include acetone, methane, and ethane (Federal 2009).

Water analysis via GC poses unique challenges. Depending on injection temperature and pressure, water expands over 1000 times in volume when injected into a GC, this expansion volume exceeds the volume of most inlet liners which causes water to

backflash into the carrier gas lines (Kuhn 2001).  Water backflash results in poor peak shape, baseline disturbances, double peaks, or ghost peaks during subsequent runs.

The NCASI methods recommend a 30 meter or longer, 0.53 mm internal diameter (ID), 3.0 um film, DB-624 (6% cyanopropylphenyl 94% dimethyl polysiloxane) or equivalent wall coated open tubular (WCOT) column connected to a GC equipped with cryogenic cooling (NCASI 2010).  Liquid nitrogen or liquid carbon dioxide cools the oven below ambient temperature which facilitates separation of water from the volatile compounds.  While some GCs have a cryogenic connection most do not.

The NCASI method allows for alternate column use provided adequate separation of compounds is attained.  Porous layer open-tubular (PLOT) columns have high retention for volatiles because, unlike WCOT columns where retention is based on polar-non-polar interactions, PLOT column retention is based on adsorption onto solid particles (Ji et al. 1999).  The high retention of volatiles eliminates the use of cryogenic cooling (Grob and Barry 2004).  There are a variety of capillary PLOT columns available for use, but porous polymer columns composed of divinylbenzene (DVB) copolymers are very hydrophobic and appropriate for water analysis (Scott and Phillips 1965; Hollis and Hayers 1966).  A new manufacturing process bonds the particles to the column wall to improve mechanical and temperature stability, and inertness (Ji et al. 1999).  Column life is short for non-bonded columns when used for water and alcohol samples (Scott and Phillips 1965); whereas bonded columns do not show degradation (Ji et al. 1999).  There are three porous polymer columns available, from least to most polar: Q (polystyrene-DVB, 280°C), S (DVB-pyridine, 250°C), and U (DVB-ethylene glycol dimethylacrylate,

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190°C).  Water retention increases on more polar columns (Hollis and Hayers 1966);

water elutes before methanol at 60°C on Q-bond columns (Ji et al. 1999).

The primary objective of this study was to determine the release of HAPs and

VOCs when drying green SP lumber to 8% MC using three kiln schedules.  To address

this, charges of lumber, as required in the Federal Register, were dried and the results are

reported herein (Federal 2006).  Methanol and formaldehyde were collected, analyzed,

and reported using the NCASI 98.01 method.  The results from these two methods satisfy

the EPA OTM-26 method (EPA 2007).  While acetaldehyde, acrolein, and

propionaldehyde have less than optimal recovery rates with the 98.01 method they were

also collected and analyzed.  Secondary objectives of the study were to determine if

relatively knotty material had increased HAP emissions and to develop a gas

chromatograph method that does not use cryogenic cooling in order to separate water

from the HAPs and other volatiles condensed from the kiln exhaust.

**Materials and Methods**

<u>Drying Procedure</u>

Green rough cut SP 51 mm x 152 mm (2x6-inch) lumber was obtained from a local mill, transported to Mississippi State University, and stored in a cooler at 2°C until drying. To first prepare the kiln test material, approximately 305 mm of length was removed from each end of every board to eliminate any end drying that occurred during storage and handling. Next, a single 584 mm long piece was cut from each lumber section and classified as relatively clear or relatively knotty material and randomly assigned into three kiln temperatures, an elevated 99°C schedule and two high temperature schedules: 116°C and 127°C. Approximately a 25 mm long section was cut to estimate the initial MC of each board. Each kiln charge contained 15 pieces of lumber. Three runs of relatively clear material and one run of relatively knotty material were dried at each kiln temperature for a total of twelve runs.

The charges were dried in a pilot-scale kiln. The time required to dry to 19% and 8% MC was recorded to compare the 19% results to previous studies and to determine the increase of emissions when drying to below 8% MC. The kiln schedules followed that of a commercial lumber kiln and are shown in Table 6.3. In general the kiln schedules required two hours of ramping to temperature. The wet bulb depression was controlled with a mass flow controller via venting action with the quantity of air entering and thus leaving the kiln. Air velocity across the lumber was approximately 213 meters per minute. The charges were dried in a random order.

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Table 6.3    Kiln temperatures, drying times, and green starting moisture content

| Dry bulb temperature | Wet bulb temperature | < 19% MC time (hrs) | < 8% MC time (hrs) | Starting MC% |
|---|---|---|---|---|
| 99°C | 77°C | 20 | 31 | 81% |
| 116°C | 82°C | 14.75 | 19.5 | 85% |
| 127°C | 85°C | 11 | 15 | 83% |

## Air Sampling for HAPs

A sample of the kiln air was collected according to NCASI 98.01 method.  The sampling train setup consists of a stainless steel probe inserted perpendicularly into the kiln exhaust, Teflon tubing, three miniature impingers connected in series, a 0.45 liter per minute critical orifice, and a vacuum pump (Figure 6.2).  The three impingers were filled with approximately 5, 15, and 20 mL of deionized water, respectively.  Prior to each sampling period leaks checks were conducted.  Before and after each run the system flow was measured at the probe tip using a bubble meter.  The impingers were placed in an ice bath throughout each sample run.  Sampling time was approximately every two to three hours.  Following sampling the flow was again measured and the sample line was rinsed with a small amount of deionized water (5 mL).

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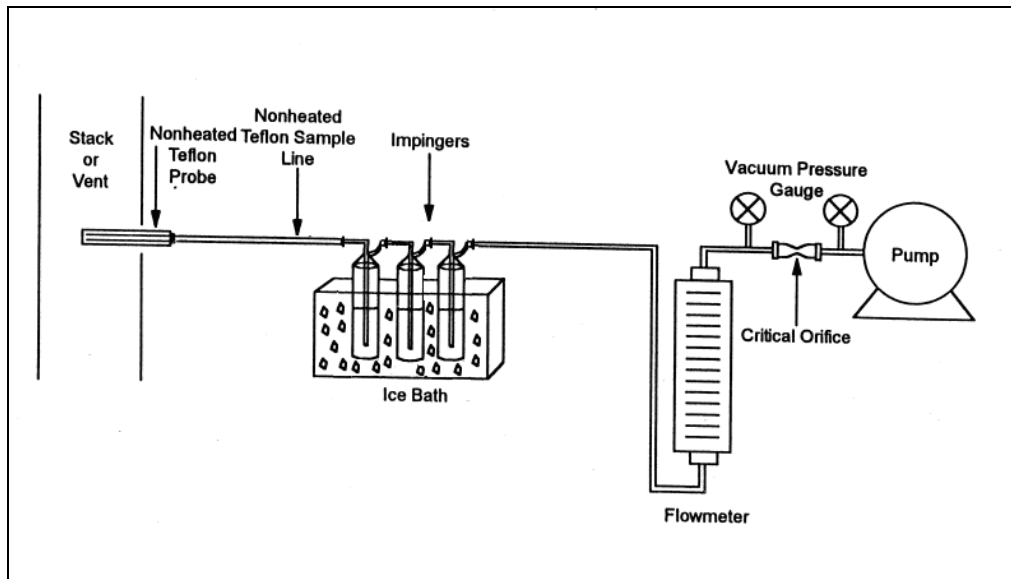
Figure 6.2    HAP sampling train setup (NCASI 1998)

Following collection of the kiln water from each sampling period, the water from the impingers was poured in a pre-weighed polyethylene vial, reweighed, and stored on ice in a cooler.  A one milliliter aliquot of the sample was transferred to an autosampler vial, capped, and stored in a refrigerator prior to gas chromatography (GC) analysis.  A two milliliter aliquot of the sample was transferred to a sampling vial and stored in a refrigerator until the sample was analyzed for formaldehyde.  Formaldehyde analysis was conducted within one week of sampling.

Several chemical recoveries were conducted using the sampling train.  To meet the requirements of the NCASI method, recovery rates must be +/- 30%.  The sampling train was assembled and the standard sampling procedures were followed.  Known calibration standards were injected into the sampling train to determine the percent chemical recovered.  The recoveries were conducted using two methods:  a single

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injection into the probe tip with subsequent three hours of sampling; and injections every fifteen minutes into the probe tip over three hours to simulate a kiln run. The target concentration for the compounds was between 1.5 to 3 ppm. The recovery of the compounds was determined based on the mass in the sampling vial versus the expected mass of each compound. Water blanks were collected and analyzed for each kiln run. Kiln blanks with stickers were also conducted and analyzed at each kiln temperature.

## PLOT Column Selection

In addition to the volatiles listed in Table 6.1, there are numerous terpenes released during kiln drying. These compounds are relatively high molecular weight compounds with low water solubility. Given that some compounds may solubilize in the condensed kiln water, we felt that the porous polymer PLOT column with the highest temperature limit would be most appropriate for use. As such, a Restek Q-bond, 30 meter, 0.53 mm ID, 20.0 um film column was evaluated for use and after careful testing the column met the needs of the analysis. The Q-bond column separated water, methanol and acetaldehyde from each other with a starting oven temperature of 85°C.

## Quantification of HAPs

Standards of each compound were prepared by diluting reagent grade compounds with organic free distilled water. The non-formaldehyde standards ranged from 1000 ppm to 0.5 ppm. Formaldehyde standards were prepared with formalin with concentrations from 0.0 ppm to 7.5 ppm. The formaldehyde stock solution was

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standardized according to the ASTM 6303-98 method, with standards stored in capped vials and refrigerated until use.

An Agilent 6890N GC equipped with electronic pressure control, flame ionization detector (FID), and a 7683 autosampler was used for the analysis. Water has the highest expansion rate among commonly used GC solvents; to minimize water backflash in the injection port and thus decrease carryover problems, a double gooseneck inlet liner was used and splitless injection volumes were limited to 0.5 uL. The column flow rate was set to 8.9 ml/min for 36 seconds to minimize backflashing of water, decreased to a constant 4.4 ml/min for 20 minutes then increased to 8.8 ml/min until the column was clean. Operating temperatures for the injection port and FID detector were held at a constant 220°C and 280°C, respectively. The oven temperature schedule was: 5 minute hold at 85°C, ramp 5°C per minute to 220°C, and hold for 55 minutes or until the column was clean. When the column was free of compounds, the oven temperature was decreased 15°C per minute to the 85°C starting oven temperature. Helium was used as the carrier gas and the detector flow rates for hydrogen and air were 30 mL/min and 400 mL/min. The nitrogen makeup and helium gas flow rates were a combined 30 mL/min. Calibration curves were developed based on actual chemical concentrations in the sample and calculated with SAS; only calibration curves with a $R^2$ higher than 0.995 were used. A sample chromatograph is shown in Figure 6.3.
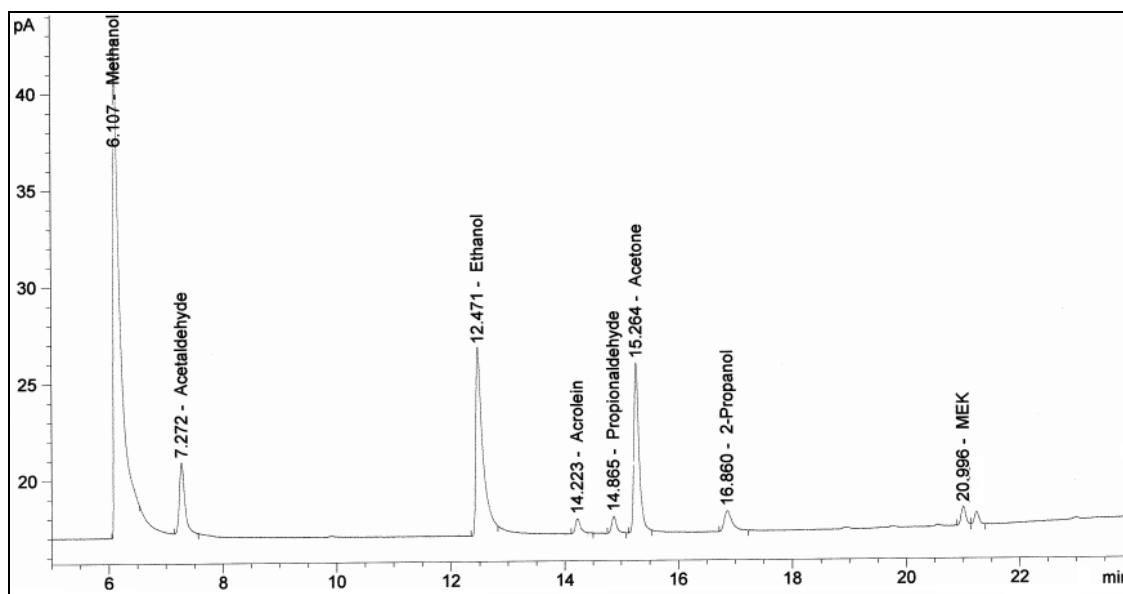
Figure 6.3    Sample chromatograph

Formaldehyde has a poor response rate with the FID detector and was analyzed on a Varian Cary 100 Bio UV-Visible spectrophotometer according to the NCASI 98.01 procedure (NCASI 1998). Formaldehyde was reacted with an acetylacetone solution in the presence of an ammonium salt to form diacetyl-dihydro-lutidine (DDL) which is yellow (Nash 1953). The solution was prepared by adding 15.4 grams ammonium acetate, 200 uL acetyl acetone, and 300 uL of aldehyde free acetic acid to a volumetric flask and diluting to 100 mL with deionized water. For each 2 mL standard or sample, 2 mL of the acetylacetone solution was added to sampling vial, placed in a 60°C water bath for 10 minutes and cooled to room temperature. The samples were transferred to a cuvette and analyzed on the spectrophotometer at the 412 nm wavelength. Following analysis the total weight of each compound was determined by scaling up the amount of air collected in the impinger train with the total amount of kiln air exhaust.

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Emissions sampling is described in the Air sampling for total VOC section found in Chapter 5 (NCASI 1998; EPA 2006).  The VOC data and the emissions of methanol, formaldehyde, and acetone were used to calculate the VOC emissions for the EPA OTM-26 method.  The total VOC data was summed with the methanol and formaldehyde emissions, and adjusted based on response rates and compound size for methanol and acetone.

## Results and Discussion

### HAP Analysis

Regarding gas chromatography analysis with the Q-Bond PLOT column, it was incredibly important to cool the oven down slowly after each analysis.  When using the standard fast oven cool down following a run during preliminary research prior to drying, during the next run the temperature ramp had numerous bleed products released which interfered with the analysis.  After some troubleshooting with the column manufacturer the cause was found to be that one side of the column was cooling down faster, this resulted in bleed products focusing on the cooler side of the column and subsequently eluting in the next run (de Zeeuw 2009).   Adding a temperature ramp of -15°C/min at the end of each run allowed the column to cool down uniformly to prevent the compounds from focusing and thus eluting in the next run.  Following this method of slowly cooling down the column after each run, the method proved reliable.  With injections limited to 0.5 uL there were no problems associated with water buildup or sample carryover.  The GC samples were analyzed immediately following each collection period to minimize compound degradation.  However, following sampling and storage in the refrigerator we

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found that the compounds were relatively stable when stored in the capped autosampler vial. After twenty days acrolein had degraded by 12% while the other compounds were still stable.

While the Q-bond PLOT columns have many advantages over WCOT columns with regard to volatile separation, the higher amounts of film thickness result in increased column bleed and long elution times for high molecular compounds. This was not an issue for the analysis because the focus was on the volatile compounds associated with lumber drying, but a laboratory interested in using this column for quantifying phenol from composite facilities would need to explore alternate GC conditions. A laboratory could save time by ballistic heating of the oven after acetone elutes or by backflushing the column using a flow switching system. Perhaps a flow switching system could also be used to switch the flow from a FID to a mass spectrometer (MS) after water elutes from the column. This potentially could result in formaldehyde being detected via GC/MS instead of colorimetrically; however more work is required to determine if this is practical.

Chemical recovery depended on the procedure used to calculate recovery and is shown in Table 6.4. Methanol and formaldehyde were within acceptable recovery ranges, but the other aldehydes recoveries generally decreased as sampling time increased. The method of capturing acetaldehyde, propionaldehyde, and acrolein using strictly water in chilled impingers is not valid because of the less than optimal stability/recovery rates; however the compounds are still recovered in the sampling procedure. The three hour recovery for acetaldehyde, propionaldehyde and acrolein was generally poor, especially with acrolein. However, during the recovery that simulated a

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kiln run by having injections every fifteen minutes for three hours the acetaldehyde, acrolein, and propionaldehyde recoveries improved greatly, although acrolein was still not within +/- 30%.

Table 6.4    Chemical recovery of compounds

| Chemical | 3 Hr recovery | Standard every 15 minutes for 3 HRs |
|---|---|---|
| Methanol | 109% | 107% |
| Formaldehyde | 85% | 95% |
| Acetaldehyde | 44% | 76% |
| Acrolein | 10% | 53% |
| Propionaldehyde | 41% | 75% |
| Ethanol | 95% | 123% |
| Acetone | 74% | 97% |
| 2-propanol | 90% | 103% |
| MEK | 61% | 89% |

The emissions of HAPs from the knotty charges were within 5% of the clear charges for each kiln schedule (data not shown).  Because of the similar results it is reasonable to conclude that overall knots had little to no effect on HAP release and so the results for the knotty and clear charges were combined to eliminate redundancies during comparisons between temperatures.  No chemicals were detected in any of the water/equipment blanks and the 99°C kiln blank with stickers.  There was a small amount of acetone (<0.75 ppm in the impingers) found in the kiln blanks with stickers in the 116°C and 127°C schedules.

<u>HAP Results Drying to 19% MC</u>

The results for the HAPs and other volatiles released when drying SP from green to 19% MC content with the combined clear and knotty charges grouped together is

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shown in Table 6.5.  Also included in the table are the emissions of ethanol, acetone, 2-propanol, and MEK.  The methanol and formaldehyde emissions from the 116°C  and 127°C schedules were significantly higher than the 99°C  schedule using an analysis of variance test (p=0.0195, p=0.0034).  All other compounds had no significant differences between the three schedules.  All three schedules had similar methanol emissions as the NCASI (2002) studies at 113°C.  The 116°C and 127°C schedules had similar releases of formaldehyde and all three schedules had lower levels of acetaldehyde and higher levels of acrolein compared to the NCASI (2002) 113°C and the Shmulsky and Dahlen (2008) study at 116°C and 127°C.  All three studies had higher amounts of propionaldehyde than the NCASI 113°C study.  The levels of formaldehyde and acetaldehyde were lower while levels of acrolein were higher when compared to the federal register.  Similar to McDonald et al. (2004), ethanol emissions were greatest at the beginning of the run and declined thereafter.

Table 6.5    Emissions from drying SP lumber from green to 19% MC (lb chemical/MBF)

| Chemical | 99°C | 116°C | 127°C |
|---|---|---|---|
| Methanol | 0.205 (B) | 0.253 (A) | 0.244 (A) |
| Formaldehyde | 0.007 (B) | 0.014 (A) | 0.017 (A) |
| Acetaldehyde | 0.032 | 0.038 | 0.032 |
| Acrolein | 0.010 | 0.012 | 0.012 |
| Propionaldehyde | 0.006 | 0.005 | 0.004 |
| Ethanol | 0.130 | 0.195 | 0.071 |
| Acetone | 0.126 | 0.123 | 0.113 |
| 2-propanol | 0.014 | 0.013 | 0.013 |
| MEK | 0.003 | 0.003 | 0.002 |

Note: statistical differences are indicated with different letters

Based on these results, a SP lumber facility would become a major source of HAPs from their methanol emissions.  Provided the kiln schedule, operation and raw

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materials were similar, a facility would reach 10 tons of methanol when drying more than 97.6, 79.1, and 82.0 million board feet per year for the 99°C, 116°C, and 127°C schedules respectively.

<u>HAP Results Drying to 8% MC</u>

The results for the HAPs released when drying SP from green to below 8% MC with the combined clear and knotty charges grouped together is shown in Table 6.6. Also included in the table are the emissions of ethanol, acetone, 2-propanol, and MEK. The methanol emissions from the 116°C and 127°C schedules were significantly higher than the 99°C schedule (p-value = 0.0032). As temperature increased the level of formaldehyde significantly increased (p-value = <0.0001). There was no significant difference with regard to acetaldehyde while acrolein emission at 127°C were significantly greater than at 99°C (p-value = 0.007). Propionaldehyde had the opposite trend of methanol where the 99°C schedule had significantly greater emissions than the 116°C and 127°C schedules (p-value=0.05); as did MEK (p-value = 0.0025). .

Table 6.6    Emissions from drying SP lumber from green to 8% MC (lb chemical/MBF)

| Chemical | 99°C | 116°C | 127°C |
|---|---|---|---|
| Methanol | 0.300 (46%) B | 0.356 (41%) A | 0.380 (56%) A |
| Formaldehyde | 0.011 (52%) C | 0.021 (41%) B | 0.029 (72%) A |
| Acetaldehyde | 0.047 (45%) | 0.050 (33%) | 0.045 (40%) |
| Acrolein | 0.013 (33%) B | 0.015 (29%) AB | 0.016 (39%) A |
| Propionaldehyde | 0.009 (50%) A | 0.007 (35%) B | 0.006 (46%) B |
| Ethanol | 0.146 (12%) | 0.218 (12%) | 0.089 (24%) |
| Acetone | 0.172 (37%) | 0.153 (25%) | 0.148 (31%) |
| 2-propanol | 0.019 (36%) | 0.017 (27%) | 0.017 (38%) |
| MEK | 0.005 (87%) A | 0.004 (52%) B | 0.004 (71%) B |

Note: increase from 19% to 8% MC in parenthesis
Statistical differences are indicated with different letters
MEK is methyl ethyl ketone

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The rate of HAP release increases greatly when lumber is dried from 19% to 8% MC.  Overall HAPs increased 44% during the time period from drying from 19% to 8%.  This is consistent with previous studies that showed that as the moisture content of the wood decreases evaporative cooling of the wood also decreases which leads to high rates of thermal degradation and thus greater HAP emissions.  Methanol, formaldehyde and MEK were the chemicals most affected by drying to 8%.  The rate of HAP emissions increased considerably higher than the VOC emissions, which only increased an average of 25% when drying from 19% to 8% MC.

Based on these results, a SP facility would become a major source of HAPs from the methanol emissions if they dried more than 66.7, 56.2, and 52.6 million board feet per year for the 99°C, 116°C, and 127°C schedules provided the kiln schedule, operation and raw material was similar.  However, it is likely that a mill will not dry all of their material to below 8%, so individual mills will reach the methanol emissions at different volumes based on their drying mixtures.  It is critical that mills do not over dry their lumber because of the spike in HAP emissions when drying to 8% MC.

<u>VOC Data</u>

The maximum ppmv values during all of the charges did not exceed the span calibration gas and the VE-7 drift did not exceed the allowable tolerances and cause data loss.  All leak checks were passed.

Table 6.7 lists the average VOC emissions as carbon for the different kiln charges.  Also included in Table 6.7 is data from previous studies that quantified SP VOC emissions from lumber.  The relatively clear charges had results typical from previous

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studies on SP lumber.  There was no significant difference between the three kiln

schedules for the relatively clear charges when drying to below 19% or 8% MC (p-value

= 0.8975, 0.8867).  The knotty charges for the 116°C and 127°C schedules were similar

to previous results for knotty southern pine lumber.  The knotty charge for the 99°C

schedule was lower than previous results and similar to clear lumber values; perhaps the

lower kiln temperature factored into this difference.

Table 6.7    VOCs emitted from green SP lumber drying to below 19% and 8% MC (lb VOC/MBF)

| Charge | NCASI VOC 19% | NCASI VOC 8% | OTM-26 VOC 19% | OTM-26 VOC 8% |
|---|---|---|---|---|
| 99°C relatively clear | 3.74 | 4.56 | 3.83 | 4.69 |
| 116°C relatively clear | 3.95 | 4.67 | 4.08 | 4.87 |
| 127°C relatively clear | 3.83 | 4.89 | 3.96 | 5.12 |
| SP sapwood (Ingram et al. 2000) | 3.83 | | | |
| SP (Milota 2006) | 3 to 4 | | | |
| 99°C relatively knotty | 3.45 | 4.40 | 3.53 | 4.53 |
| 116°C relatively knotty | 5.71 | 6.90 | 5.84 | 7.06 |
| 127°C relatively knotty | 5.66 | 7.54 | 5.77 | 7.71 |
| SP knotty (Ingram et al. 2000) | 5.46 | | | |

Drying from 19% to 8% MC resulted in an average additional 1.1 pounds of

VOCs emitted per thousand.  The greatest VOC increase occurred with the relatively

knotty material at 127°C where an additional 1.88 pounds per thousand of VOCs were

released.  The VOC results from the OTM-26 method are slightly higher (2-5%) than the

NCASI method because of the more accurate methanol analysis.

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The VOC, methanol and formaldehyde emissions were similar to previous studies with regard to drying below 19% MC. The results with regards to HAP release from 19% to 8% MC were similar to previous studies that showed that as moisture content decreased HAPs tended to increase. At conventional temperatures acetaldehyde emissions from lumber have been shown to be equal to or greater than methanol emissions, but this was not the case with the 99°C elevated schedule. It would be interesting to see if the same trend would occur for southern pine; however, the schedules used in this study were more practical for southern pine than an 82°C schedule. We had some concerns with lumber degrade when drying from 19% to 8% MC, but degrade was minimal for all three schedules.

The aldehyde stability in water over a three hour time period is low, particularly acrolein and, thus the more recent NCASI methods recommend a one hour sampling time and utilize more sampling equipment/derivatization to further capture the aldehydes. Surprisingly, even with the poor aldehyde stability found with the water only method, acrolein and propionaldehyde emissions were greater than previous studies using the newer methods. The higher levels of acrolein and propionaldehyde may have been the result of analyzing the samples directly following analysis. It appears that with better recovery of acetaldehyde the results would have been more similar to previous studies.

In all three schedules, regardless of drying to 19% or to 8%, a mill would reach 10 tons of methanol before reaching 25 tons from the total HAPs. Higher kiln temperatures resulted in greater emissions of methanol and formaldehyde. It is critical with regard to limiting HAP emissions that mills do not over dry the lumber. Currently the EPA's HAP

ruling treats all chemicals equally with regard to emission limits; however, if the ruling changed such that higher risk compounds are more highly regulated then SP mills would need to focus more on acrolein emissions.

## Literature Cited

Agency for Toxic Substances and Disease Registry (ATSDR). 1990. Toxicological Profile for Acrolein. Public Health Service, U.S. Department of Health and Human Services, Atlanta, GA.

Calabrese, E.J. and E.M. Kenyon. 1991. Air Toxics and Risk Assessment. Lewis Publishers, Chelsea, MI.

Department of Health and Human Services (HHS). 1993. Hazardous Substances Data Bank. National Toxicology Information Program, National Library of Medicine, Bethesda, MD.

Department of Health and Human Services (HHS). 2005. 11th Report on Carcinogens. National Toxicology Program. Section 301(b)(4), Section 262, PL 95-622.

de Zeeuw, J. 2009. Personal communication. August 3, 2009.

Environmental Protection Agency (EPA). 1996. Method 0011 – Sampling for selected aldehyde and ketone emissions from stationary sources. United States Environmental Protection Agency. Washington, DC.

Environmental Protection Agency (EPA). 2006. Method 25A – Determination of Total Gaseous Organic Concentration Using a Flame Ionization Analyzer. United States Environmental Protection Agency. Washington, DC.

Environmental Protection Agency (EPA). 2007. Method OTM-26. Interim VOC Measurement Protocol for the Wood Products Industry – July 2007. United States Environmental Protection Agency. Washington, DC.

Federal Register. 2006. National Emission Standards for Hazardous Air Pollutants: Plywood and Composite Wood Products; List of Hazardous Air Pollutants, Lesser Quantity Designations, Source Category List; Final Rule. February 16, 2003, Rules and Regulations. 71(32): 8342-8387.

Federal Register. 2007. National Emission Standards for Hazardous Air Pollutants: Plywood and Composite Wood Products. October 29, 2007, Rules and Regulations. 72(208): 61060-61063.

Federal Register. 2009. Volatile Organic Compounds. July 1, 2009. 40 CFR Part 51.100(s): 139-140.

Grob, R.L., and E.F. Barry. 2004. Modern Practice of Gas Chromatography. John Wiley & Sons, Inc. Hoboken, New Jersey. pp. 1036.

Hollis, O.L., and W.V. Hayers. 1966. Water Analysis by Gas Chromatography Using Porous Polymer Columns. Journal of Gas Chromatography 4: 235-239.

Ingram, L.L. Jr, R. Shmulsky, A.T. Dalton, F. W. Taylor, and M. Curry Templeton. 2000. The measurement of volatile organic emissions from drying southern pine lumber in a laboratory-scale kiln. Forest Products Journal 50(4):91-94.

Ji, Z., R.E. Majors, and E.J. Guthrie. 1999. Porous layer open-tubular capillary columns: preparations, applications and future directions. Journal of Chromatography A, 842: 115-142.

Kuhn, Eberhardt. 2001. Water injection in gas chromatography: Part 1. Separation Times. Agilent Technologies. 14(1): pp.10-11.

Law, R. 2009. Personal Communication. December 4, 2009.

McDonald, A.G., J.S. Gifford, D. Steward, P.H. Dare, S. Riley, I. Simpson. 2004. Air emission from timber drying: high temperature drying and re-drying of CCA treated timber. Holz als Roh- und Werkstoff 62:291-302.

Milota, M.R. 2005. Hazardous air pollutants: what they mean to a Sawmill. Proceedings of the 55th Annual Meeting. Western Dry Kiln Assocation: 85-89.

Milota, M.R. 2006. Hazardous air pollutant emissions from lumber drying. Forest Products Journal 56(7/8): 79 – 84.

Milota, M. and P. Mosher. 2006. Emissions from western hemlock lumber during drying. Forest Products Journal 56(5):66-70.

Milota, M. and P. Mosher. 2008a. A comparison of methods for measuring hazardous air pollutants from lumber dry kilns. Forest Products Journal 58(7/8):46-49.

Milota, M. and P. Mosher. 2008b. Emissions of hazardous air pollutants from lumber drying. Forest Products Journal 58(7/8):50-55.

Nash, T. 1953. The colorimetric estimation of formaldehyde by means of the hantzsch reaction. Biochemical Journal (55): 416-421.

National Council for Air and Stream Improvement (NCASI). 1998 (estimated). Standard protocol for VOC concentration measurement method for use at small-scale kilns. Gainesville, Florida.

National Council for Air and Stream Improvement (NCASI). 2002. A comparative study of VOC emissions from small-scale and full-scale lumber kilns drying southern pine. Technical Bulletin #845. NCASI, Gainesville, Florida.

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National Council for Air and Stream Improvement (NCASI). 2010. NCASI methods manual. http://www.ncasi.org/publications/toc/default.aspx?id=6. Accessed 8-24-2010.

Otwell, L.P., M.E. Hittmeir, U. Hooda, H. Yan, W. Su, and S. Banerjee. 2000. HAPs released from wood drying. Environmental Science and Technology (34): 2280-2283.

Schafer M. and E. Roffael. 2000. On the formaldehyde release of wood. Holz als Roh- und Werkstoff 58:259-264.

Shmulsky, R. and J. Dahlen. 2008. "Acrolein and selected HAPS from southern pine: a comparison of four mills." Quality Drying for the 21st Century: Energy and Market Realities. Forest Products Society: 191-198.

Scott, C.G. and C. Phillips. 1965. Gas chromatography 1964. Institute of Petroleum. London. pp. 266.

Su W., H. Yan, S. Banerjee, L.P. Otwell, and M. Hittmeier. 1999. Field-proven strategies for reducing volatile organic carbons from hardwood drying. Environmental Science and Technology 33:1056-1059.

APPENDIX A

CHAPTER V & VI:  VOC PPM CONVERSION TO VOC POUNDS PER 1,000

BOARD FEET

Total flow rate (TFR): measured air flow rate of hydrocarbon analyzer sampling train with the dilution system turned off.

Sample flow rate (SFR): measured air flow rate of hydrocarbon analyzer sampling train with the dilution system turned off.

Instrument response (IR): response of VOC analyzer expressed as ppm of propane.

Undiluted wet stack concentration (SC): Undiluted response for the sample gas at the probe tip.

$$SC = IR \times \frac{PRE\_TFR + POST\_TFR}{PRE\_SFR + POST\_SFR} \times \frac{3carbons}{1propane} \tag{A.1}$$

Vapor pressure of water depending on the wet bulb temperature (e).

Wet bulb temperature (WBT): Fahrenheit.

$$e = 6.087 \times 10^{-6} \times WBT^3 - 1.00431 \times WBT^2 + 0.0756 \times WBT - 1.693 \tag{A.2}$$

Absolute barometric pressure (ABP): in. Hg.

Dry bulb temperature (DBT): Fahrenheit.

Moisture content of the exhaust gas (MCkiln): Determined using the Oregon Method 4.

$$MCki\ln = \frac{e - \dfrac{(ABP - e)(DBT - WBT)}{2800 - 1.3 \times WBT}}{ABP} \times 100 \tag{A.3}$$

Dry entering air flow rate (dcfm): The dry entering air flow rate in cubic feet per minute which equals the volume of standard dry air leaving the kiln.

Wet entering air flow rate (wcfm): The wet exhaust flow rate leaving the kiln.

$$WCFM = DCFM \times \frac{100}{100 - MCki\ln} \qquad (A.4)$$

Conversion of SC and WSCFM to pounds VOC as carbon per minute:

$$\frac{lbs\_VOC\_as\_carbon}{\min ute} = \frac{SC}{10^6} \times wcfm \times \frac{1\_lb\_mole}{385.6 scf} \times \frac{12\_lb\_carbon}{lb\_mole} \quad (A.5)$$

Conversion of pounds VOC as carbon per minute to pounds of carbon per minute per 1000 board feet:

$$\frac{lbs\_VOC\_as\_carbon\_per\_MBF}{\min ute} = \frac{lbs\_VOC\_as\_carbon}{\min ute} \times \frac{1000\_bd\_feet}{bd\_feet\_ch\arg e} \qquad (A.6)$$

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APPENDIX B

CHAPTER VI:  CHEMICAL PPM CONVERSION TO CHEMICAL POUNDS PER

1,000 BOARD FEET

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Total water weight (TWW) in g.

Post sampling bottle weight (PSBW) in g.

Empty bottle weight (EBW) in g.

$$TWW = PSBW - EBW \qquad \text{(B.1)}$$

Total water weight (g) = post sampling bottle weight (g) - empty bottle weight (g).

Correct sampling flow rate (CSFR) in L/min.

Average flow rate (AFR) in L/min

Average barometric pressure (ABP) in mm HG

Saturated partial pressure of water vapor (SPPWV) in mm HG

Average Temperature (AT in C.

$$CSFR = AFR * \left( ABP - \frac{SSPPWV}{760} * \frac{293}{273 + AT} \right) \qquad \text{(B.2)}$$

Flow rate factor (FRF).

Correct sampling flow rate (CSFR) in L/min.

Total kiln flow rate (TKFR) in L/min.

$$FRF = CSFR * TKFLW \qquad \text{(B.3)}$$

Chemical weight impingers (CWI) in ug.

Chemical ppm (CPPM) in (ug/mL).

$$CWI = CPPM * TWW \qquad \text{(B.4)}$$

Total chemical weight (TCW) in ug.

$$TCW = CWI * FRF \qquad \text{(B.5)}$$

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Chemical pounds per minute (CPPM) in lb/min.

Sampling time (ST) in min.

$$CPPM = TCW * ST$$
(B.6)

Chemical pounds per minute per thousand board feet (CPMMBF) in lb/min.

Board feet in kiln charge (BFKC) in board feet.

$$CPPMBF = CPPM * \frac{1000}{BFKC}$$
(B.7)

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