Chemistry of Thermal Treatment

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Wood Chemistry

• Wood is a lignocellulosic material
  – Term based on its chemical ‘construction’

• Three main constituents (% of dry wood weight)
  – Cellulose 40-45%
  – Hemicellulose(s) 25-35%
  – Lignin 20-25%

• Minor components
  – Extractives 2-5%
  – Ash (proteins, inorganics) ½-1%
Cellulose

- What is it?
  - 1→4 β-D-glucopyranose
  - Linear polymer of glucose molecules
  - Degree of polymerization (molecules in polymer)
    8,000 to 11,000
  - Long chains of cellobiose (glucose + flipped glucose)
Cellulose

• Organization
  – Cellulose chains bond to adjacent chains (hydrogen bonds and van der Waals forces) to form ‘elementary fibrils’ and larger ‘microfibrils’
  – The spatially ordered structure leads to regions of crystallinity in the cellulose and higher order organizations of cellulose chains
Biosynthesis of Cellulose

Cellulose synthase complex

Rosette subunit

Rosette (in plasma membrane, microfibril deposited onto the cell wall)

Individual cellulose chain

Cellulose microfibril
Cellulose

- **Degree of Crystallinity**
  - Cellulose microfibrils are crystalline (at least partially, ~40-70%)
  - Crystallinity = mechanical strength, resistance to biological attack
Hemicellulose(s)

• Structure
  – Similar to cellulose, well-defined enzyme controlled synthesis but not crystalline
  – Branched, more hydrophilic (more readily adsorb water than cellulose)
  – Differ between hardwoods and softwoods
    • Hardwoods highly acetylated

Hardwood xylan (glucuronoxylan)
15-30% of dry weight
Lignin

• Structure
  – Amorphous structure
  – 3 basic subunits that combine randomly (in 3D) through radical-radical coupling reactions
Lignin

- Structure continued
Lignin
Chemistry Summary

• Cellulose

  - Linear polymer, 40-70% crystalline in wood
Chemistry Summary

• Hemicellulose

in wood cell wall 50 of these connected linearly

— Linear but also branched, amorphous
Chemistry Summary

• Lignin

– Amorphous, irregular
Chemistry Summary

Water in Wood

Hemicellulose
Cellulose
Lignin

More hydrophilic

Less hydrophilic
Chemistry Summary

Water in Wood

Hemicellulose  
More hydrophilic  
More accessible hydroxyl groups

Cellulose  
Less hydrophilic  
Less accessible hydroxyl groups

Lignin  

Lignin has tons of phenolic hydroxyl groups but not as accessible as polysaccharides.

Hydrogen bond
Chemistry Summary

Hemicellulose

Less thermally stable

Cellulose
Lignin

More thermally stable
Chemistry Summary

• What is the chemical ‘architecture’ of cell wall
  – We know the cell wall in wood is composed of a multiple layers
    • Wood tracheid (6-20 GPa)
  – The cellulose microfibrils impart strength and stiffness to the cell wall
    • Rebar (130-140 GPa)
  – Hemicellulose bonds with lignin (lignin carbohydrate complex) and also with cellulose
    • Poured concrete (3-8 GPa)
  – Lignin ‘encrusts’ the polysaccharide components
    • Concrete masonry unit (2-7 GPa)
Ultrastructure

Possible chemical architecture

inner layer ($S_1$)

middle layer ($S_2$)

outer layer ($S_3$)

primary wall

Lignin

Hemicellulose - Arabinoglucuronoxylan

Hemicellulose - Galactoglucomannan

Cellulose
Chemistry Summary

• How does it look in wood?
  – Maybe like this: or this:
Chemistry Summary

• How does it look in wood?
  – Or maybe like this:

Or this:
How does it look in wood? – Or maybe like this:

- **Extractives**
  - Long chain fatty acids
  - Triglycerides
  - Resin acids
  - Terpenes

- **Cell wall components**
  - Lignin
  - Hemicellulose - Arabinoglucuronoxylan
  - Hemicellulose - Galactoglucomannan
  - Cellulose
Chemistry Summary

Wood cell wall

inner layer ($S_3$)

middle layer ($S_2$)

outer layer ($S_1$)

primary wall

20 - 40 $\mu$m
Thermal Treatment Overview

- Treatment temperature 160-260°C (320-500°F)
  - Flame point: 225-260°C (437-500°F) gases formed from wood decomposition will ignite
  - Burn point: 260-290°C (500-554°F) wood will steadily burn with flame

- Must remove oxygen to prevent burning
  - Shielding gases (N₂)
  - Water vapor
  - Vacuum

- Mass loss a general indicator of quality
  - 2-12% is typical for commercial treatments
Thermal Treatment Overview

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gases formed from wood decomposition will ignite
- Burn point: 260–290°C (500–554°F) wood will steadily burn
- Must remove oxygen to prevent burning
- Shielding gases (N2), water vapor

- Mass loss a general indicator of quality
  - 2–12% is typical for commercial treatments
  - 4–6% limit for EMC reduction

![Graph showing mass loss over treatment time at different temperatures](image-url)
Thermal Treatments Outcomes

• Positive attributes
  – Reduced hygroscopicity (EMC)
  – Improved dimensional stability
  – Darkening
  – Improved durability (resistance to biodegradation)

• Decay organisms attack via hemicellulose, amorphous regions of cellulose, degradation products condense on lignin ‘confusing’ fungal enzymatic system
  – (Possible inhibitory compounds formed, but extraction of thermally treated wood doesn’t affect durability)
Thermal Treatments Outcome

• Negative attributes
  – Reduced surface energy (lower OH availability)
    • Poor gluability, paintability
  – Splits, cracks, loose knots, etcetera
    • Need high grade lumber
  – Reduced mechanical properties
    • Abrasion, toughness, work to maximum load, strength, modulus of elasticity, hardness, impact bending
      – Possible increase MOE (hornification [H\(^+\), covalent bonding])
Thermal Treatment Processes

• Many different commercial methods (all European)
  – Treatment temperature 160-260°C (320-500°F)
  – Temperature rise, thermal treatment stage, cooling and equilibration stage

• Thermowood (Finland)
  – Heat and vapor, green or dry lumber,
  – 180-250°C treatment temperature

• Plato wood (Netherlands)
  – Heat and vapor, green lumber
  – 160-190°C treatment temperature
Thermal Treatment Processes

• Retification (France)
  – Heat and nitrogen, dry lumber
  – 200-240°C treatment temperature
• Le Bois Perdure (France)
  – Heat and wood vapors, green lumber
  – 200-250°C treatment temperature
• Oil Heat Treatment (Germany)
  – Heat and crude vegetable oil, green lumber
    • Mass increases, oil adsorbed
  – 180-220°C treatment temperature
Thermal Treatment Process

• Chemical changes are occurring during two stages of thermal treatment

• Drying stage <150°C (<302°F)

followed by

• Thermal treatment stage <260°C (<500°F)

Very generalized, treatments vary greatly
Thermal Treatment Process

• Thermal treatment stage time varies

• Influenced by specific gravity, MC, initial temperature, target temperature, board dimensions, heat transfer medium (shielding gas, steam)
  – Hours to many hours
Drying Stage <150°C (<302°F)

• Moisture loss from wood
  – Free water followed by bound water

• Loss of volatile extractives
  – Monoterpenoids (α-pinene, β-pinene)
  – Acids (acetic, formic, propionic)

• Net effect is minor
  – Extractives are nonstructural
Thermal Treatment Stage <260°C (<500°F)

- Water pKa decreases with temperature

- It’s becoming a stronger acid
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

- Acetyl groups cleaved by hydrolysis → acetic acid generated
  - Acetic acid can break glycosidic bonds along hemicellulose backbone or amorphous cellulose (especially in steam treatments)

Hardwood xylan (glucuronoxylan)
15-30% of dry weight
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

- HWs have higher mass loss compared to SWs
  - HW hemicellulose more acetylated (7Ac per 10Xy)
  - SW hemicellulose less acetylated (1Ac per 4Glc)

Hardwood xylan (glucuronoxyylan)
15-30% of dry weight

Softwood glucomannan
15-20% of dry weight
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose

- Removal of ‘water of constitution’
- Loss of hydroxyl (-OH) groups

Degradation products lost as VOCs
Thermal Treatment Stage <260°C (<500°F)

Effects on Hemicellulose

- Degrade into furfural, hydroxymethylfurfural, and subsequent degradation products

Acids = equipment corrosion

Acetic acid

Formic acid

Furfural also responsible for ‘smoky’ odor
Thermal Treatment Stage <260°C (<500°F) Effects on Hemicellulose Summary

- Deacetylation
  - Acetyl groups removed
- Dehydration
  - Loss of water of constitution
- Depolymerization
  - Glycosidic bonds broken along xylose chain
- Reduced hygroscopicity
  - Loss of hydroxyl bonding sites
  - Residual degradation products (furfural, hydroxymethylfurfural) less hydrophilic
Thermal Treatment Stage <260°C (<500°F) Effects on Cellulose Summary

• Crystalline regions unchanged
  – Stable to 300°C

• Amorphous region degraded
  – Less so compared to hemicelluloses

• Degree of crystallinity increases
  – Crystalline remains, amorphous degraded
  – No amorphous regions are converted
Lignin is thermoplastic
- Will plasticize and physically flow, rearrange
  - $T_g = 150°C$

Condensation reactions, cross-linking
- Lignin structure condenses within itself
- Degradation products of hemicellulose condense onto lignin macrostructure
- Contributes to color changes
Thermal Treatment Stage <260°C (<500°F) Effects on Lignin

- Softwood lignin more modified
  - SW lignin less condensed, HW S and G type lignin, SW predominantly G type lignin

[Chemical structures of Guaiacyl (G) and Syringyl (S) lignin subunits]
Reduced hygroscopicity – Hemicellulose and amorphous cellulose regions degraded, fewer available bonding sites (–OH) – Residual degradation products (furfural, hydroxymethylfurfural) less hydrophilic

Mechanical properties reduced – Cellulose remains largely intact, crystalline regions not affected by thermal conditions – Hemicellulose degradation prevents transfer of stress from rigid cellulose to amorphous lignin

Wood becomes more brittle

Thermal Treatment Effect on Wood Properties

Fig. 4. SEM images on longitudinal tangential surfaces of specimens before and after artificial weathering: (a) untreated and before weathering; (b) heat-treated at 195 °C and before weathering; (c) heat-treated at 215 °C and before weathering; (d) untreated and after weathering of 72 h; (e) heat-treated at 195 °C and after weathering of 72 h; (f) heat-treated at 215 °C and after weathering of 72 h; (g) untreated and after weathering of 672 h; (h) heat-treated at 195 °C and after weathering of 672 h; (i) heat-treated at 215 °C and after weathering of 672 h; (j) untreated and after weathering of 1512 h; (k) heat-treated at 195 °C and after weathering of 1512 h; (n) heat-treated at 215 °C and after weathering of 1512 h.

Fig. 3. SEM images (×5000) on transverse s after 1512 h of artificial weathering: (a) untreated after weathering; (c) heat-treated at 195 °C at 195 °C after weathering; (e) heat-treated treated at 215 °C after weathering.
Embrittlement

Modulus of Elasticity = stiffness

Modulus of Rupture = strength

Green at start of thermal treatment vs dry at start of thermal treatment

0-20% reduction

5-35% reduction
Thermal Treatment Process Variables

• Open versus closed system
  – Closed systems will result in higher mass loss due to the concentration of acids released from wood
  – Closed systems also result in higher pressure due to dissolved degradation products
• Wet versus dry systems
  – Wet systems result in higher mass loss
    • More protons more hydrolysis
• Air versus shielding gases
  – Thermal treatment in air results in greater mass loss as result of oxidation reactions
• Temperature and time
  – Longer times and higher temperatures result in greater mass loss
• Dimensions and species of boards
  – Initial MC, density, heat transfer
Thermal Treatment Summary

• Chemical changes during thermal treatment result in reduced hygroscopicity resulting in desirable EMC reduction, increased durability, and improved dimensional stability

• Chemical changes during thermal treatment result in decreased mechanical properties
Weathering of Thermally Modified

Fig. 1. Visual appearance of tangential surfaces of birch, untreated and heat-treated at different temperatures during weathering: (a) untreated, (b) heat-treated at 195°C, (c) heat-treated at 205°C, (d) heat-treated at 215°C.
Acetylated Wood

• Wood treated with acetic anhydride
  – Acetate groups replace hydroxyl (-OH) and acetyl (OCH₃) groups in wood cell wall
  – Acetic acid released