# Wood Products: Thermal Degradation and Fire

Wood is a thermally degradable and combustible material. Applications range from a biomass providing useful energy to a building material with unique properties. Wood products can contribute to unwanted fires and be destroyed as well. Minor amounts of thermal degradation adversely affect structural properties. Therefore, knowledge of the thermal degradation and fire performance of wood can be critical in many applications. Chemical treatments are available to improve fire performance characteristics.

## 1. Thermal Degradation

As wood reaches elevated temperatures, the different chemical components undergo the thermal degradation that affects the performance of wood. The extent of the changes depends on the temperature level and length of time under exposure conditions. Permanent reductions in strength can occur at temperatures $> 65°C$, with the amount depending on the temperature, pH of wood, moisture content, heating medium, exposure period, and species. Strength degradation is likely to be due to depolymerization reactions involving no significant carbohydrate weight loss. Research on chemical mechanisms has found a kinetic basis (involving activation energy, pre-exponential factor, and order of reaction) of relating strength reduction to temperature. Chemical bonds begin to break at temperatures $> 100°C$ and are manifested as carbohydrate and lignin weight losses of various types that increase with the temperature (wood pyrolysis). Literature reviews on thermal degradation can be found in Bryden (1998), Miller and Bellan (1996), Shafizadeh (1984), Atreya (1983), and Browne (1958).

### 1.1 Temperature Regimes of Wood Mass Loss

Thermal degradation above $100°C$ can be broken up into four temperature regimes:

(i) Between $100°C$ and $200°C$, wood becomes dehydrated and generates water vapor and other noncombustible gases and liquids including $CO_2$, formic acid, acetic acid, and $H_2O$. With prolonged exposures at higher temperatures, wood can become charred. Exothermic oxidation reactions can occur because ambient air can diffuse into and react with the developing porous char residue.

(ii) From $200°C$ to $300°C$, some wood components begin to undergo significant pyrolysis, and in addition to the gases and liquids listed previously, significant amounts of CO and high-boiling-point tar are given off. The hemicelluloses and lignin components are pyrolyzed in the ranges $200–300°C$ and $225-450°C$, respectively (see Wood, Constituents of). Much of the acetic acid liberated from wood pyrolysis is attributed to deactylation of hemicellulose. Dehydration reactions around $200°C$ are primarily responsible for pyrolysis of hemicellulose and lignin and results in a high char yield for wood. Although cellulose remains mostly unpyrolyzed, its thermal degradation can be accelerated in the presence of water, acids, and oxygen. As the temperature increases, the degree of polymerization of cellulose decreases further, free radicals appear, and carbonyl, carboxyl, and hydroperoxide groups are formed. Bryden (1998) assumed tar undergoes cracking to lighter gases and repolymerization to char while streaming through the hot charred residue. Overall pyrolysis reactions are endothermic due to decreasing dehydration and increasing CO formation from porous char reactions with $H_2O$ and $CO_2$ with increasing temperature. During this "low-temperature pathway" of pyrolysis, exothermic reactions of exposed char and volatiles with atmospheric oxygen are manifested as glowing combustion.

(iii) The third temperature regime is from $300°C$ to $450°C$ because of the vigorous production of flammable volatiles. This begins with significant depolymerization of cellulose in the range $300–350°C$. Also, around $300°C$ aliphatic side chains start splitting off from aromatic rings in the lignin. Finally, the carbon–carbon linkage between lignin structural units is cleaved from $370°C$ to $400°C$. The degradation reaction of lignin is an exothermic reaction, with peaks occurring between $225°C$ and $450°C$. The temperatures and amplitudes of these peaks depend on whether samples were pyrolyzed under nitrogen or air. All wood components end their volatile emissions at around $450°C$. The presence of minerals and moisture within the wood tends to smear the separate pyrolysis processes of the major wood components. In this "high-temperature pathway," pyrolysis of wood results in overall low char residues of around 25% or less of original dry weight. Many fire retardants work by shifting wood degradation to the "low-temperature pathway," which reduces volatiles available for flaming combustion.

(iv) At $> 450°C$, the remaining wood residue is char, which undergoes further degradation by being oxidized to $CO_2$, CO, and $H_2O$. This is referred to as afterglow.

### 1.2 Kinetic Parameters of Wood Pyrolysis

The complex nature of wood pyrolysis often leads to the selection of empirical kinetic parameters of wood pyrolysis applicable to specific cases. Considering the degrading wood to be at low elevated temperature for a long period and ignoring volatile emissions, a simple

first-order reaction following the Arrhenius equation was found practical:

$$\frac{dm}{dt} = Am \exp\left(-\frac{E}{RT}\right)$$

where $m$ is the mass of the specimen, $t$ is time, A is the pre-exponential factor, $E$ is the activation energy, $R$ is the universal gas constant, and T is the temperature in kelvin. The simplest heating environment for determination of these kinetic parameters is isothermal, constant pressure, and uniform flow gas exposures on a nominally thick specimen. As an example, Stamm (1955) reported mass loss of coniferous wood sticks (25 mm by 25 mm by 150 mm; southern and white pine, Sitka spruce, and Douglas fir) that were heated in a drying oven over a temperature range of 93–250°C. The fit of Arrhenius equation to data resulted in values of $A = 6.23 \times 10^7 s^{-1}$ and $E = 124 kJmol^{-1}$. When these wood sticks were exposed to steam instead of being oven dried, degradation was much faster, with corresponding kinetic parameters of $A = 82.9 s^{-1}$ and $E = 66 kJmol^{-1}$. Stamm concluded that steam acted as a catalyst because of significant reduction in the value of the activation energy. Shafizadeh (1984) showed that pyrolysis proceeds faster in air than in an inert atmosphere and that this difference gradually diminishes around 310 °C. Values of activation energy reported for pyrolysis in air varies from 96 to 147 kJ mol$^{-1}$.

In another special case, a simple dual reaction model could distinguish between the low- and high-temperature pathways for quantifying the effect of fire retardant on wood pyrolysis (Tang 1967):

$$\frac{dm}{dt} = (m_{end} - m)$$

$$\times \left[ A_1 \exp\left(-\frac{E_1}{RT}\right) + A_2 \exp\left(-\frac{E_2}{RT}\right) \right]$$

In this equation, $m_{end}$ is the ending char mass, and subscripts 1 and 2 represent low- and high-temperature pathways, respectively. Dynamic thermogravimetry was used to span the temperature to 500°C at a rate of 3°C min$^{-1}$ using very small wood particles of ponderosa pine sapwood, lignin, or alpha-cellulose samples with five different inorganic salt treatments. Tang's derived values for the untreated wood were $m_{end} = 0.21$ of initial weight, $A_1 = 3.2 \times 10^5 s^{-1}$, $E_1 = 96 kJmol^{-1}$, $A_2 = 6.5 \times 10^{16} s^{-1}$, and $E_2 = 226 kJ mol^{-1}$.

A well-known flame-retardant-treatment (FRT) chemical, monoammonium phosphate, was the most effective tested in that char yield was increased to 40%

and $E_1$ decreased to 80 kJ mol$^{-1}$, thereby promoting volatile loss through the low-temperature pathway. Alpha-cellulose reacted to the chemicals in a similar manner to the wood, and lignin did not seem to be affected much by the chemicals. Thus, these FRT chemicals significantly reduced the flammable volatiles generated by the cellulose component of wood. Potential FRT chemicals are often initially tested using dynamic thermogravimetry or differential scanning calorimetry. The FRT chemical monoammonium phosphate has also been found to have the most effect on strength properties of wood exposed to elevated temperatures > 65 °C.

For applications to biomass energy and fire growth phenomenology, kinetic parameters become essential to describe flammable volatiles and their heat of combustion, but are very complicated. Using a sophisticated pyrolysis model, Bryden (1998) showed that to maintain a uniform temperature profile at very high temperatures under isothermal or uniform rate of temperature rise conditions, the wood particles are required to be less than a fraction of a millimeter. In thermogravimetric analysis, this small size factor is not a difficulty, except that the pyrolysis is no longer realistic. This is because in real applications: (i) evaporating moisture creates high pressures resulting in Darcy flow of steam and volatiles in the thick porous wood, (ii) tar decomposes when passing through porous char, and (iii) heating rate is both locally high and low so that all four regimes of the wood pyrolysis are involved in a single wood slab.

Pyrolysis models such as those of Bryden (1998) and Miller and Bellan (1996) include competing reactions to produce char, tar, and noncondensing gases from wood as well as the secondary reaction of tar decomposition. Bryden's model incorporates reactions of $CO_2$, CO, and $H_2O$ with char to form CO gas that converts to $CO_2$ during glow combustion. Miller and Bellan's model uniquely obtains "robust" pyrolysis of the wood components, hemicellulose, lignin, and cellulose, such that various oven-dried wood species can be accommodated without changing the constants. Uses of such sophisticated models are limited by their numerous empirical kinetic and thermophysical parameters, certain phenomenology incompleteness, and large computation times.

## 2. Fire Performance Properties of Wood

In building applications, fire performance of wood and other combustible materials are regulated based on performance in standard tests. Although improvements have been made in standard tests for fire performance, results of such tests are only applicable for fire exposure and other conditions of the standard test. In this section, the fire performance of wood is reviewed in the context of general fire performance and regulatory tests.

## 2.1 Ignition

Ignition of wood is the start of visual and sustained combustion (smoldering, glow, or flame) fueled by wood pyrolysis. Therefore, the flow of energy or heat flux from a fire or other heated object to induce pyrolysis is a necessary condition of ignition. Sufficient conditions of flaming ignition are the mixing together of combustible volatiles and air in the right composition and a temperature from 400°C to 500°C. An ignition source (pilot flame or spark plug) is therefore usually placed where optimum mixing of volatiles and air can occur for a given ignition test. In such tests, the surface temperatures of wood materials have been measured in the range 300-400°C prior to piloted ignition. This coincides with the third regime of wood pyrolysis in which there is a significant production of flammable volatiles. However, it is possible for smoldering or glowing to exist prior to flaming ignition if the imposed heating causes the wood surface to reach 200°C or higher for the second regime of wood pyrolysis. From tests that imposed a constant external heat flux to the wood surface, values for ignition temperature, minimum flux needed for ignition, and thermophysical properties have been derived. Density and moisture content have a large influence on these material-dependent properties. Critical heat flux for ignition has been calculated to be between 10 and 13kWm$^{-2}$ for a range of wood products. For exposure to a constant heat flux, ignition times for solid wood typically ranged from 3s for heat flux of 55kWm$^{-2}$ to 930s for heat flux of 18kWm$^{-2}$.

Unpiloted ignition is flaming ignition that occurs in the absence of a pilot source. The external heat flux needed for unpiloted ignition is around 25kWm$^{-2}$, depending on the apparatus. For radiant heating of cellulosic solids, unpiloted transient ignition has been reported at 600°C. With convective heating, unpiloted ignition has been reported as low as 270°C and as high as 470°C. Unpiloted ignition that involves wood exposed to low level external heat sources for very long periods is in dispute. Schaffer (1980) used a residual weight criterion of 40% of the initial weight to suggest that wood can safely be heated to 150°C for a year or more. This temperature criterion is based on the assumption that thermal degradation is a necessary condition for such ignition. Evidence that such a low temperature criterion is a sufficient condition for ignition has not been successfully documented. Temperatures as low as 70°C are recommended for wood exposed for long periods to prevent significant permanent loss of properties as well as prevent ignition.

A special type of unpiloted ignition is spontaneous ignition that occurs when heat generated from an internal source is not readily dissipated. Such ignition generally occurs for a prolonged period and involves smoldering. Continuous smoking is visual evidence of smoldering, which is sustained combustion within the pyrolyzing material. Although smoldering can be initiated by an external ignition source, a particularly dangerous smoldering is that initiated by internal heat generation. In order of increasing temperature, potential mechanisms include respiration, metabolism of microorganisms, adsorptive heat, heat of pyrolysis, and abiotic oxidation. If such internal heat generation is sustained by a continuous supply of fresh air and sufficiently contained by the material's thermal insulation, internal temperatures will continuously increase, leading first to smoldering and sometimes further to flaming ignition. Examples of such fires include panels or paper removed from a press or dryer and stacked in large piles without adequate cooling and very large piles of chips or sawdust subjected to exothermic biological activities.

## 2.2 Rate of Heat Release

Heat of combustion measured in an oxygen bomb calorimeter is the total heat available. Higher heating values for wood are about 20kJkg$^{-1}$. Heat of combustion depends on the relative lignin and holocellulose and extractive contents of wood. Cellulose and hemicellulose have a higher heating value of 18.6kJkg$^{-1}$, whereas lignin has a higher heating value of 23.2–25.6kJkg$^{-1}$. Higher heating values of extractives are about 32–37kJ kg$^{-1}$.

In a fire situation, the contribution of combustible materials to a fire depends more on the rate of heat release (RHR) rather than the total heating value. The best known method for determining RHR is the American Society of Testing Materials (ASTM) E1354 (also ISO 5660), known as the cone calorimeter which is based on the oxygen consumption method. With untreated wood, the RHR increases to a peak shortly after ignition, then decreases to a lower semiconstant RHR when exposed to a constant heat flux. The char layer provides thermal insulation from the fire and gradually reduces the rate of charring propagation, thus also the RHR. Wood specimens tested with an insulating backing will also have a second peak in RHR due to termination of the thermal wave and the afterglow phenomena. In general, the averaged effective heat of combustion in cone calorimeter tests of wood is about 65% of the higher heating value from an oxygen bomb.

## 2.3 Charring

Wood charring is the primary factor that determines the load-carrying capacity of structural wood members in a fire. In a fully developed fire, the base of the char layer is generally assumed to be at approximately 300°C. When a quasisteady-state charring rate is obtained, the temperature beneath the char layer can be expressed as an exponential or a power term for thick wood. The temperature gradient is steep with a

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temperature of 180°C only 6 mm inward from the base of the char layer. For a given heat flux exposure, the charring rate of wood depends on its density, moisture content, chemical composition, and permeability. For external heat fluxes of 18–55 kWm$^{-2}$, the charring rate ranges from 2.6 to 0.8 min mm$^{-1}$.

## 2.4 Flame Spread

Flame spread is the sliding movement of the flaming ignition point over the surface of a solid combustible. Thus, the flame foot provides the ignition source as well as mixing of volatiles and air. The quasisteady time response of the material to heat flux distribution from the flame and external sources in reaching the surface temperature of rapid volatilizations (coinciding with a point of ignition at around 300°C depending on the wood species) determines the rate of flame spread. Rate of flame spread generally decreases with increases in density, moisture content, surface emissivity, surface temperature at ignition, and thermal conductivity. It increases with the magnitude of heat exposure from the flame. This makes upward or ceiling flame spread (along the airflow direction) a serious fire safety issue because of the accelerating potential to room flashover with the attendant high rate of heat release and smoke and toxic gas production. In contrast, downward or lateral flame spread (opposite to airflow direction) has heating from the adjoining flame of such a small extent that external heat sources are required to sustain the flame spreading on wood products. For most building applications, the regulatory test for building material acceptance in North America is the flame spread test known as the "25 ft" (7.6 m) tunnel (ASTM E84). Most untreated wood products have a Flame Spread Index of 60–190 in the ASTM E84 tunnel test. A wide range of flammability test methods is used for regulatory purposes in other countries and for research and development.

## 3. Flame-retardant Treatment of Wood

Most flame-retardant treatments delay ignition, reduce heat release, and reduce flame spread. As discussed previously, many flame-retardant chemicals shift the thermal degradation to the low temperature pathway of noncombustible gases and a greater proportion of char residue. The reactions are acid-catalyzed hydrolysis of the cellulose and hemicellulose. Chemicals dehydrate the wood and increase the condensation and cross-linking of the carbon skeleton. Other possible mechanisms for fire retardancy include formation of an insulating layer, increased dissipation via conduction of heat away from heat source, endothermic reactions to absorb heat, and release of radicals that inhibit flaming combustion.

For interior applications where leaching is not an issue, water-soluble inorganic salts are the common flame retardants. These salts include monoammonium and diammonium phosphate, ammonium sulfate, zinc chloride, sodium tetraborate, and boric acid. These chemicals are combined in formulations to develop optimum fire performance (flaming, smoldering, and smoke) yet still retain acceptable hygroscopicity, strength, corrosivity, and other properties. For example, boric acid is often added to reduce smoldering or glowing. Another chemical used in interior formulations is guanylurea phosphate. For a leach-resistant system, one method is to polymerize the fire-retardant resins after impregnation into the wood. Such a treatment is the amino resin system based on urea, melamine, dicyandiamide, and related compounds.

A major class of flame-retardant coatings includes those that intumesce to form an expanded low-density protective film upon exposure to fire. Intumescent formulations include a dehydrating agent, a char former, and a blowing agent. Potential dehydrating agents include polyammonium phosphate. Ingredients for the char former include starch, glucose, and dipentaerythritol. Potential blowing agents for the intumescent coatings include urea, melamine, and chlorate paraffin. Performance requirements can be found in the standards of the American Wood Preservers' Association. Flame-retardant-treated wood has a Flame Spread Index of less than 25 in ASTM E84 used in North America. Flame-retardant treatments generally reduce the initial peak heat release, average heat release, and the effective heat of combustion. Ignition times are often increased. Excessive levels of flame-retardant treatment can increase the production of smoke. Flame-retardant treatments tend to have minimal impact on charring rates and the fire endurance of structural members.

Wood treated with inorganic flame-retardant salts can be more hygroscopic than untreated wood. The increases in equilibrium moisture content will depend upon the chemical, level of chemical retention, and size and species of wood involved. A higher moisture content increases problems with corrosion of fasteners. Applications that involve high humidity require treated wood designed for low hygroscopicity. Flame-retardant treatment of wood generally results in reductions in the mechanical properties of wood. Flame-retardant-treated wood is often more bash than untreated wood. Some fire-retardant formulations can cause further losses in strength with continued exposure to elevated temperatures found in roof applications. Such losses occur when the fire-retardant salts catalyze the acid hydrolysis of the holocellulose at elevated temperatures much lower than that associated with a fire.

## 4. Concluding Remarks

Issues of thermal degradation and fire performance are often overlooked in the use of wood because of its ease of use. In situations of elevated temperatures or

direct fire exposure, an understanding of the thermal degradation and fire behavior of wood is needed. Although considerable research has been done on its thermal degradation and fire behavior, the complexity of the processes involved leaves many gaps in gaining a full understanding of thermal degradation and fire behavior of wood.

See also: Wood Products: Aging of Wood; Wood Products: Chemical Degradation; Wood: Strength and Stiffness; Wood: Thermal Properties

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R. H. White and M. A. Dietenberger