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Thermal Degradation

When wood is exposed to elevated temperatures, changes can occur in its chemical structure that affect its performance. The extent of the changes depends on the temperature level and the length of time under exposure conditions. The changes in chemical structure may be manifested only as reduced strength, and hygroscopic water and volatile oil weight loss. In contrast, very drastic chemical changes may result in reduced strength and significant carbohydrate weight loss.

At temperatures below 100°C, permanent reductions in strength can occur. The magnitude of the reduction depends on the moisture content, heating medium, exposure period and species. The strength degradation is usually not considered to result from the same thermal decomposition of the wood that occurs above 100°C, since no significant carbohydrate weight loss occurs. The strength degradation is probably due to depolymerization reactions, although little research has been done on the chemical mechanism. Reviews by Gerhards (1979, 1982, 1983) and Koch (1985) summarize reduction in strength at temperatures below 100°C (See *Strength*). If the wood has been treated with a chemical to reduce its flammability, more significant reductions in strength can occur at lower temperatures than for untreated wood. This is due to the presence of chemicals that catalyze the dehydration and depolymerization reactions. A review by Winandy (1987) summarizes the effects of elevated temperatures on strength properties of treated wood.

At temperatures above 100°C, chemical bonds begin to break. The rate at which the bonds are broken increases as the temperature increases. Between 100°C and 200°C, noncombustible products, such as carbon dioxide, traces of organic compounds and water vapor, are produced. Above 200°C the celluloses break down, producing tars and flammable volatiles that can diffuse into the surrounding environment. If the volatile compounds are mixed with air and heated to the ignition temperature, combustion reactions occur. The energy from these exothermic reactions radiates to the solid material, thereby propagating the combustion, or pyrolysis, reactions. If the burning mixture accumulates enough energy to emit radiation in the visible spectrum, the phenomenon is known as flaming combustion (see *Fire and Wood*). Above 450°C all volatile material is gone. The residue that remains is an activated char that can be oxidized to carbon dioxide, carbon monoxide and water vapor. Oxidation of the char is referred to as afterglow.

The thermal degradation of wood can be represented by two pathways (Fig. 1), one occurring at high

temperatures (>300°C), the other at lower temperatures. These two competing reactions occur simultaneously. Fire retardants work by shifting degradation to the low-temperature pathway.

1. Thermal Degradation of Wood Components

The thermal degradation of wood can be represented as the sum of the thermal degradation reactions of the individual components, namely cellulose, hemicellulose and lignin. However, the thermal degradation reactions of wood itself can vary from the sum of the individual-component reactions. Therefore, this discussion on thermal degradation includes analysis of the individual components and wood itself.

1.1 Cellulose

Cellulose is principally responsible for the production of flammable volatiles. Degradation occurs through dehydration, hydrolysis, oxidation, decarboxylation and transglycosylation.

By the low-temperature pathway, water is evolved from oven-dried cellulose, and the cellulose shows a large decrease in its degree of polymerization. The thermal degradation of cellulose 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. Thermal degradation rates increase as heating continues.

The primary reaction of the high-temperature pathway is depolymerization. This takes place when the cellulose structure has absorbed enough energy to activate the cleavage of the glycosidic linkage to produce glucose, which is then dehydrated to levoglucosan (1, 6-anhydro-β-D-glucopyranose) and oligosaccharides. The glycosidic linkages are hydrolyzable

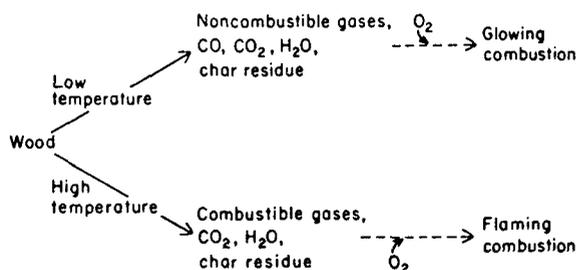


Figure 1
Degradation of wood by low-temperature and high-temperature pathways

at room temperature in the presence of strong acids. During pyrolysis, water and acids are produced from both the hemicellulose and the cellulose.

As temperature increases to around 450°C, the production of volatile compounds is complete. The continuing weight loss is due to degradation of the remaining char.

1.2 Hemicelluloses

Hemicelluloses are less stable thermally than cellulose and evolve more noncombustible gases and less tar. Most hemicelluloses do not yield significant amounts of levoglucosan. Much of the acetic acid liberated from wood pyrolysis is attributed to deacetylation of the hemicellulose. Hardwood hemicelluloses are rich in xylan and contain a small amount of glucomannan. Softwood hemicelluloses contain a small amount of xylan and are rich in galactoglucomannan. Of the hemicelluloses, xylan is the least thermally stable, because pentosans are most susceptible to hydrolysis and dehydration reactions. The hemicelluloses degrade at temperatures from 200°C to around 260°C.

1.3 Lignin

Pyrolysis of lignin yields phenols from cleavage of ether and carbon-carbon linkages and produces more residual char than does pyrolysis of cellulose. The structure of lignin has been investigated using mass spectrometry to determine various lignin pyrolysis products. Dehydration reactions around 200°C are primarily responsible for thermal degradation of lignin. Between 150°C and 300°C, cleavage of α - and β -aryl-alkyl-ether linkages occurs. Around 300°C, aliphatic side chains start splitting off from the aromatic ring. Finally, the carbon-carbon linkage between lignin structural units is cleaved at 370–400°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 the samples were pyrolyzed under nitrogen or air.

1.4 Wood

The influence of the individual components on the thermal degradation reactions of wood can be seen by plotting percentage weight loss as a function of temperature for the components and for wood itself (Fig. 2). The degradation of holocellulose, which consists of the alpha-cellulose plus the hemicelluloses, most closely follows that of wood. Lignin generally pyrolyzes at a slower rate than cellulose and holocellulose, although the degradation period begins somewhat earlier than for the holocellulose. Also, the presence of lignin increases the residual weight of the final char product. Alpha-cellulose and wood appear to degrade at similar rates, although wood begins to degrade at slightly lower temperatures than alpha-cellulose but higher temperatures than holocellulose. This lower degradation temperature of wood is pri-

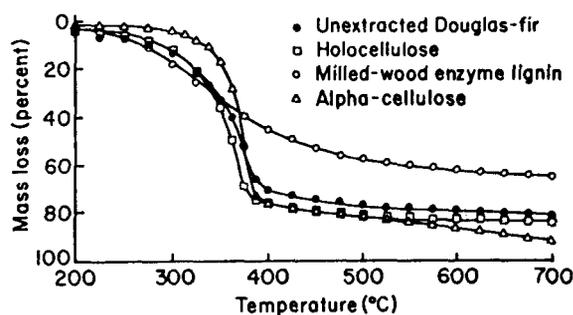


Figure 2
Mass losses of isolated Douglas-fir wood components heated in nitrogen at 5°C min⁻¹

marily due to the hemicelluloses in the wood and holocellulose. The wood degradation resembles more closely the degradation pattern of the alpha-cellulose and holocellulose than the degradation pattern of the lignin. This is reasonable because cellulose and holocellulose account for approximately 50% and 75% of the wood, respectively.

2. Kinetic Parameters of Thermal Degradation

The temperatures at which decomposition reactions of wood occur and the changes in specimen weight associated with the reactions can be found by thermogravimetric analysis. Quantitative methods can be applied to the thermogravimetric analysis curves (Fig. 2) to obtain kinetic parameters of thermal degradation, which govern the reaction rates. The kinetic parameters usually include the activation energy, the preexponential factor and the order of reaction. Typically, these describe the rate of mass loss and the heat of combustion of the volatiles. They are also useful in describing the temperature dependence of the mass loss rate. However, these kinetic parameters are highly dependent on experimental conditions such as heating rates, sample size and atmosphere and thus should only be considered as effective kinetic parameters having no physical significance. A wide range of values has been reported for both the activation energy and the preexponential factor, assuming a simple first-order reaction following the Arrhenius equation:

$$\dot{m} = A \exp(-E/RT)$$

where \dot{m} is the mass loss rate, A the preexponential factor, E the activation energy, R the universal gas constant and T the temperature in kelvin. Independent measurements have been made on the individual wood components and wood itself. The following values are listed here only to indicate the range to be expected. These values were determined by different methods under different conditions and at different heating rates, and therefore they are not directly comparable.

The degradation of cellulose can be analyzed as a first-order Arrhenius equation. Effective activation energies for cellulose pyrolyzed in nitrogen have been found to range from 170 to 210 kJ mol⁻¹ (Hirata 1979, Tang 1967). Effective activation energies for pyrolysis in air are lower, ranging from 109 to 151 kJ mol⁻¹ (Akira 1979, Shafizadeh 1984, Stamm 1955). Some have reported that wood and alpha-cellulose degradation follow a two-step first-order decomposition.

The activation energy for hardwood xylan pyrolyzed in nitrogen ranges from 75 to 164 kJ mol⁻¹. Beall (1969) reported values for the activation energy around 13 kJ mol⁻¹ for softwood xylan and around 34 kJ mol⁻¹ for softwood glucomannan.

Activation energy values for lignin vary depending on the isolation procedures used to obtain the lignin. Beall (1969) and Tang (1967) determined activation energies of 46 and 88 kJ mol⁻¹, respectively, for lignin processed in sulfuric acid. Parker and LeVan (1988) determined an activation energy of 122 kJ mol⁻¹ for milled-wood enzyme lignin. Ramiah (1970) found activation energies of 55 kJ mol⁻¹ for periodate lignin and 80 kJ mol⁻¹ for Klason lignin.

Activation energies for wood pyrolyzed in nitrogen range from 63 to 139 kJ mol⁻¹ for pyrolysis temperatures less than 300°C and from 109 and 227 kJ mol⁻¹ for temperatures greater than 300°C. For pyrolysis in air, the values range from 96 to 147 kJ mol⁻¹. Shafizadeh (1984) showed that pyrolysis proceeds faster in air than in an inert atmosphere and that this difference gradually diminishes around 310°C. Atreya (1983) found this difference to disappear around 400°C.

See also: Thermal Properties

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