6 Thermal Properties

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The traditional question at the start of a class on thermal properties of wood is, “Does wood burn?” The students have all been warmed in front of a wood-burning fire before, so they are sure the answer is yes—but since the professor asked the question, there must be some hidden trick to the obvious answer. Going with their experience, their answer is “yes, wood burns.” But, the actual answer is no, wood does not burn. In short, wood undergoes thermal degradation as it heats up, giving rise to volatile, flammable gases which burn when they contact a source of ignition. So it is the flammable gases that burn, not the wood itself. This is, of course, an oversimplified explanation of the pyrolysis and burning processes which are the subject of this chapter.

Lignocellulosic materials decompose on heating and when exposed to an ignition source by two different mechanisms. The first, dominant at temperatures below 300°C, degrades polymers

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by the breaking of internal chemical bonds; dehydration (elimination of water); formation of free radicals, carbonyl, carboxyl, and hydroperoxide groups; formation of carbon monoxide and carbon dioxide; and finally, the formation of reactive carbonaceous char. Oxidation of the reactive char results in smoldering or glowing combustion, and further oxidation of the combustible volatile gasses gives rise to flaming combustion (Antal 1985, Bridegwater 1999, Czernik et al. 1999, Shafizadeh 1984).

The second mechanism, which takes over at temperatures above 300°C, involves the cleavage of secondary bonds and formation of intermediate products such as anhydromonosaccharides, which are converted into low molecular weight products (oliosaccharides and polysaccharides), which lead to carbonized products (Kawamoto et al. 2003).

6.1 PYROLYSIS AND COMBUSTION

The simplest method of evaluating the thermal properties of wood is by thermogravametric analysis (TGA). Figure 6.1 shows a schematic of the equipment used for this analysis. A sample is placed in a metal pan in a furnace tube. Nitrogen gas is passed through the system and the furnace tube is slowly heated at a constant rate. The percent of weight loss is measured as function of temperature and is printed out on a strip chart. The temperature is usually raised to 500–600°C in nitrogen at a rate of a few degrees Celsius per minute. The temperature is then lowered to around 300°C, oxygen is introduced into the system, and the temperature is increased again. This second scan shows the combustion of the char in oxygen.

A simple thermogram run in nitrogen is shown in Figure 6.2 for pine (Shafizadeh 1984). As the wood is heated from room temperature to 100°C, very few chemical reactions take place. At approximately 100°C, any moisture in the wood is vaporized out. As the temperature of the wood increases, very little degradation occurs until about 200°C, when chemical bonds start to break via dehydration and, possibly, free radical mechanisms to eliminate water and produce volatile gases. In the absence of oxygen, or in the presence of limited amounts, this thermal degradation process

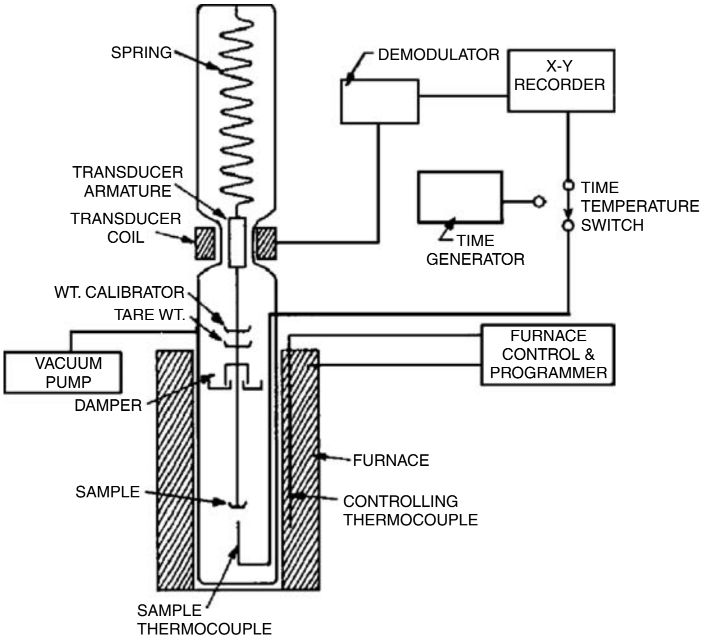

FIGURE 6.1 Schematic diagram of a simple thermogravimetric analysis system.

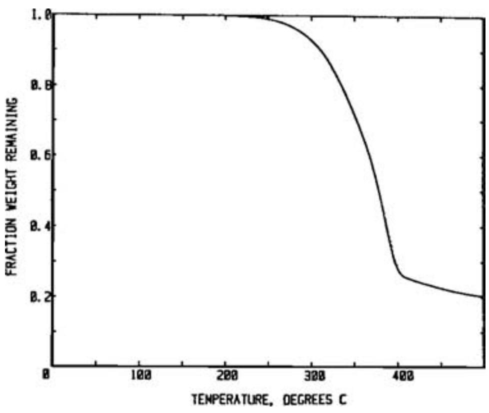

FIGURE 6.2 Thermogravimetric analysis of pine.

is called *pyrolysis*. The volatile gases produced diffuse out of the wood into the surrounding atmosphere. Figure 6.3 shows the first derivative of the TGA curve for pine.

Whole wood starts to thermally degrade at about 250°C (see Figure 6.4). Between about 300–375°C, the majority of the carbohydrate polymers have degraded and only lignin remains. The hemicellulose components start to decompose at about 225°C and are almost completely degraded by 325°C. The cellulose polymer is more stable to thermal degradation until about 370°C, and then decomposes almost completely over a very short temperature range. Both the acid lignin and milled wood lignin start to decompose at about 200°C, but are much more stable to thermal degradation as compared to the carbohydrate polymers. The curve for whole wood represents the results of each of the cell wall components. The pyrolysis products given off when wood is thermally degraded are shown in Table 6.1 (Shafizadeh 1984).

Since the major cell wall polymer is cellulose, the thermal degradation of cellulose dominates the chemistry of pyrolysis (Shafizadeh and Fu 1973). The decomposition of cellulose leads mainly to volatile gases, while lignin decomposition leads mainly to tars and char. Figure 6.5 shows the pyrolysis and combustion of cellulose (Shafizadeh 1984). In the early stages of cellulose degradation (below 300°C), the molecular weight is reduced by depolymerization caused by dehydration reactions. The main products are CO, CO_2 produced by decarboxylation and decarbonylation, water, and char residues. In the presence of oxygen, the char residues undergo glowing ignition. CO and CO_2 form much faster in oxygen than in nitrogen, and this rate accelerates as the temperature

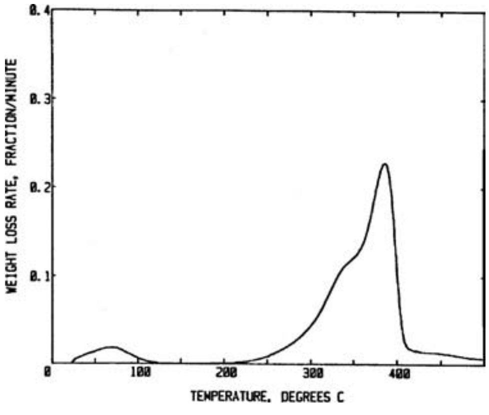

FIGURE 6.3 Derivative thermogravimetric analysis of pine.

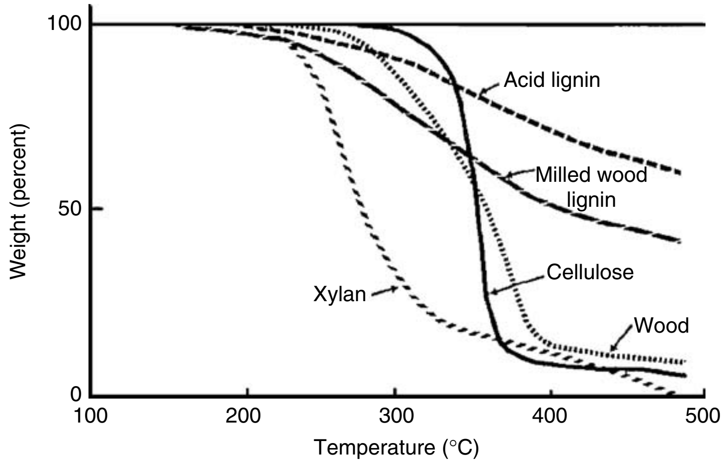

FIGURE 6.4 Thermogravimetric analysis of cottonwood and its cell wall components.

increases. Table 6.2 shows the rate constants for the depolymerization of cellulose in air and nitrogen (Shafizadeh 1984).

Cellulose also produces such combustible volatiles acetaldehyde, propenal, methanol, butanedione, and acetic acid. When the combustible volatiles mix with oxygen and are heated to the ignition temperature, exothermic combustion occurs. The heat from these reactions in the vapor phase transfers back into the wood, increasing the rate of pyrolysis in the solid phase. When the burning mixture accumulates sufficient heat, it emits radiation in the visible spectrum. This phenomenon is known as *flaming combustion* and occurs in the vapor phase. At 300°C the cellulose molecule is highly flexible and undergoes depolymerization by transglycosylation to create such products as anhydromonosaccharides, which include levoglucosan (1,6-anhydro-β-D-glyucopyranose)

TABLE 6.1
Pyrolysis Products of Wood

Product	Percent in Mixture
Acetaldehyde	2.3
Furan	1.6
Acetone	1.5
Propenal	3.2
Methanol	2.1
2,3-Butanedione	2.0
1-Hydroxy-2-propanone	2.1
Glyoxal	2.2
Acetic acid	6.7
5-Methyl-2-furaldehyde	0.7
Formic acid	0.9
2-Furfuryl alcohol	0.5
Carbon dioxide	12.0
Water	18.0
Char	15.0
Tar (at 600°C)	28.0

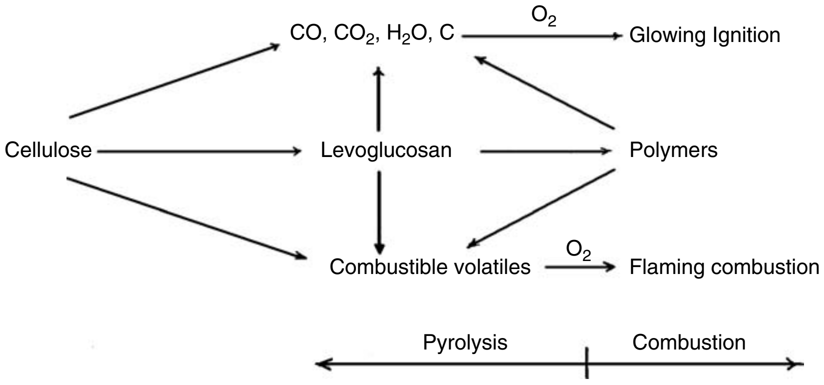

FIGURE 6.5 Pyrolysis and combustion of cellulose.

and 1,6-anhydro-β-D-glyucofuranose. These are converted into low molecular weight products, randomly linked oliosaccharides and polysaccharides, which lead to carbonized products.

Figure 6.6 shows the formation of levoglucosan from cellulose. When a single unit of cellulose (glucose) undergoes dehydration, it forms levoglucosan, levoglucosenone, and 1,4:3,6-dianhydro-α-D-glucopyranose. Products such as the 1,2-anhydride and the 1,4-anhydride, 3-deoxy-D-erythro-hexosulose, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde (furfural), other furan derivatives, 1,5-anhydro-4-deoxy-D-hex-1-ene-3-ulose, and other pyran derivatives also form (Shafizadeh 1984). These dehydration derivatives are important in the intermediate formation of char compounds.

The intermolecular and intramolecular transglycosylation reactions are accompanied by dehydration, followed by fission or fragmentation of the sugar units and disporportionation reactions in the gas phase (Shafizadeh 1982). The anhydromonosaccharides can recombine to form polymers, which can then degrade to CO, CO_2, water and char residues, or combustible volatiles.

Above 300°C, the rate of tar-forming reactions increases and the formation of char decreases. Table 6.3 shows the percent of char and tar products formed from cellulose as a function of temperature (Shafizadeh 1984). At 300°C, there are about 28% tar and 20% char products. As the

TABLE 6.2
Rate Constants for the Depolymerization of Cellulose in Air and Nitrogen

Temperature	Condition	$K_o \times 10^7$ (mol/162 g min)*
150	N_2	1.1
	Air	6.0
60	N_2	2.8
	Air	8.1
170	N_2	4.4
	Air	15.0
180	N_2	9.8
	Air	29.8
190	N_2	17.0
	Air	48.9

*One mol of glucose

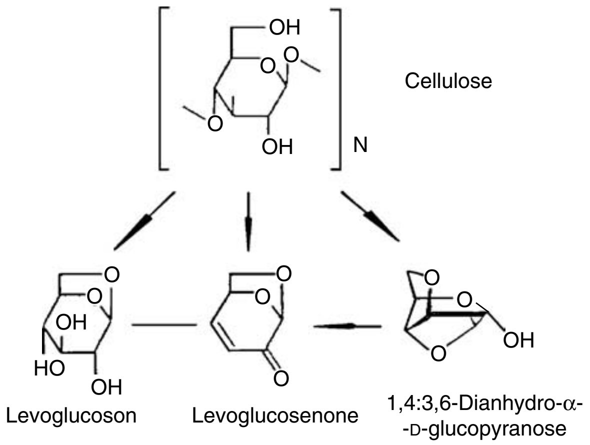

FIGURE 6.6 Formation of levogluosan and other monomers from cellulose.

temperature increases to 350°C, the tar product yield has increased to 38% and the char to 8%. At 500°C, the tar product yield has stayed about the same, but the char yield has decreased to 2%.

The tar products include anhydro sugar derivatives that can hydrolyze to reducing sugars. The evaporation of levoglucosan and other volatile pyrolysis products is highly endothermic. These reactions absorb heat from the system before the highly exothermic combustion reactions take place.

Table 6.4 shows the char yield of cellulose, wood, and lignin at various temperatures. The highest char yield for cellulose (63.3%) occurs at 325°C; by 400°C, the yield has decreased to 16.7%. The char yield for whole wood at 400°C is 24.9%, and is 73.3% for isolated lignin. The carbon, hydrogen, and oxygen analysis for the various char yields show that the highest carbon content char occurs at 500°C—but the char yield is only 8.7%. The table shows that the lignin component gives the highest char yield (Sharizadeh 1984). Lignin mainly contributes to char formation and cellulose; the hemicelluloses mainly create volatile pyrolysis products that are responsible for flaming combustion.

The intensity of combustion can be expressed as:

$$I_R = -\Delta H \frac{dw}{dt}$$

TABLE 6.3
Tar and Char Yields from Cellulose Pyrolysis at Different Temperatures

Temperature (°C)	Tar Yield (%)	Char Yield (%)
300	28	20
325	37	10
350	38	8
375	38	5
400	38	5
425	39	4
450	38	4
475	37	3
500	38	2

TABLE 6.4
Char Yield from Cellulose, Wood, and Lignin and Chemical Composition of the Char*

Material	Temperature (°C)	Char Yield (%)	Carbon Analysis (%)	Hydrogen Analysis (%)	Oxygen Analysis(%)
Cellulose	Control	—	42.8	6.5	50.7
	325	63.3	47.9	6.0	46.1
	350	33.1	61.3	4.8	33.9
	400	16.7	73.5	4.6	21.9
	450	10.5	78.8	4.3	16.9
	500	8.7	80.4	3.6	16.1
Wood	Control	—	46.4	6.4	47.2
	400	24.9	73.2	4.6	22.2
Lignin	Control	—	64.4	5.6	24.8
	400	73.3	72.7	5.0	22.3

* Isothermal pyrolysis, 5 minutes at temperature.

where:

I_R = reaction density,
$-\Delta H$ = heat of combustion
dw/dt = rate mass of fuel loss

Table 6.5 shows the heat of combustion for cellulose, whole wood, bark, and lignin. The highest level of volatiles are produced by cellulose, which has the lowest heat of combustion and the lowest percentage of char formation. The next level of volatiles are produced by whole wood, having slightly higher heat of combustion and char yield as compared to cellulose. Bark has a higher heat of combustion as compared to wood, with a char yield of 47% and 52% volatiles. Lignin has the highest heat of combustion and also the highest char yield and the lowest percent of volatiles.

The high rate of heat released upon flaming combustion provides the energy needed to gasify the remaining wood elements and propagate the fire. Oxidation of the residual char after flaming combustion results in glowing combustion. If the intensity of the heat and the concentration of combustible volatiles fall below the minimum level for flaming combustion, gradual oxidation of the reactive char initiates smoldering combustion. The smoldering combustion process releases noncombustible or unoxidized volatile products and usually occurs in low-density woods.

TABLE 6.5
Heat of Combustion of Wood, Cellulose, and Lignin, Char and Combustible Volatile Yields*

Fuel	Heat of Combustion ΔH 25 C (cal/g)	Char Yield (%)	Combustible Volatiles (%)
Cellulose	–4143	14.9	85.1
Wood (Poplar)	–4618	21.7	78.3
Bark (Douglas-fir)	–5708	47.1	52.9
Lignin (Douglas-fir)	–6371	59.0	41.0

*Heating rate 200°C/min to 400°C/min and held for 10 minutes.

FIGURE 6.7 Wood beam survives fire in casein plant in Frankfort, NY.

6.2 FIRE RETARDANCY

Wood has been used for many applications because it has poor thermal conductivity properties. In a fire, untreated wood forms a char layer—an insulation barrier protecting the wood below the burning layer (self-insulating). The comparative fire resistance of wood and metal was never more visibly demonstrated than in pictures taken after many hours of burning in the 1953 fire at a casein plant in Frankfort, New York (Figure 6.7). The steel girders softened, failed at high temperatures, and fell across the 12 × 16 inch laminated wood beams that were charred, but still strong enough to hold the steel girders.

To improve the fire resistance of wood, fire retardants have been developed. The use of fire retardants for wood can be documented back to the first century A.D., when the Romans treated their ships with alum and vinegar for protection against fire (LeVan 1984). Later, Gay-Lussac used ammonium phosphates and borax to treat cellulosic textiles. The U.S. Navy specified the use of fire retardants for their ships starting in 1895, and the City of New York required the use of fire retardants in building over twelve stories high starting in 1899 (Eickner 1966).

Building and fire codes specify fire-safety standards for structures. Building codes include area and height of the rooms, firestops, doors and other exits, automatic sprinklers, fire detectors, and type of construction. Fire codes include materials combustibility, flame spread, and fire endurance. In most residential construction, fire retardants may not be required but in public buildings, fire retardants are usually required.

6.3 TESTING FIRE RETARDANTS

6.3.1 THERMOGRAVIMETRIC ANALYSIS (TGA)

There are several ways to test the efficiency of a fire retardant. The most common is to run TGA analysis as described earlier. TGA involves weighing a finely ground sample and exposing it to a heated chamber in the presence of nitrogen. The sample is suspended on a sensitive balance that measures the weight loss of the sample as the system is heated (Figure 6.1). Nitrogen or another gas flows around the sample to remove the pyrolysis or combustion products. Weight loss is recorded as a function of time and temperature (see Figures 6.2 and 6.4). In isothermal TGA, the change in weight of the sample is recorded as a function of time at a constant temperature. With the use of a derivative computer, the rate of weight loss as a function of time and temperature can also be measured (Figure 6.3). This is referred to as *derivative thermogravimetry* (Slade and Jenkins 1966).

6.3.2 DIFFERENTIAL THERMAL ANALYSIS (DTA) AND DIFFERENTIAL SCANNING CALORIMETRY (DSC)

DTA measures the amount of heat liberated or absorbed by a wood sample as it moves from one physical transition state to another (such as melting or vaporization) or when it undergoes any chemical reaction. This heat is determined by measuring the temperature differences between the sample and an inert reference. DTA can be used to measure heat capacity, provide kinetic data, and give information on transition temperatures. The test device consists of sample and reference pans exposed to the same heat source. The temperature is measured using thermocouples embedded in the sample and the reference pan. The temperature difference between the sample and reference is recorded against time as the temperature is increased at a linear rate. For calorimetry, the equipment is calibrated against known standards at several temperatures (Slade and Jenkins 1966).

DSC is similar to DTA, except the actual differential heat flow is measured when the sample and reference temperature are equal. In DSC, both the sample and reference are heated by separate heaters. If a temperature difference develops between the sample and reference because of exothermic or endothermic reactions in the sample, the power input is adjusted to remove this difference. Thus, the temperature of the sample holder is always kept identical to that of the reference.

6.3.3 TUNNEL FLAME-SPREAD TESTS

Building standards designed to control fire growth often require certain flame-spread ratings for various parts of a building. For code regulations, flame-spread ratings are determined by a 25-foot tunnel test, which is an approved standard test method (ASTM E 84). For research, 2- and 8-foot tunnel tests can also be done. All tunnel tests measure the surface flame spread of the wood, although each differs in the method of the exposure. A specimen is exposed to an ignition source, and the rate at which the flames travel to the end of the specimen is measured. In the past, red oak flooring was used as a standard and given a rating of 100.

The severity of the exposure and the time a specimen is exposed to the ignition source are the main differences between the various tunnel test methods. The 25-foot tunnel test, where the specimen is exposed for 10 minutes, is the most severe exposure. An extended test of 30 minutes is performed on fire-retardant treated products. Because the 25-foot tunnel test is the most severe exposure, it is used as the standard for building materials. The 2-foot tunnel test is the least severe, but because small specimens can be used, it is a valuable tool for development work on fire retardants. Table 6.6 shows average values for the flame spread index of several wood species (White and Dietenberger 1999).

6.3.4 CRITICAL OXYGEN INDEX TEST

The oxygen index test measures the minimum concentration of oxygen in an oxygen-nitrogen mixture that will just support flaming combustion of a test specimen. Highly flammable materials have a low oxygen index, and less flammable materials have high values (White 1979). One advantage of this test is that very small specimens can be used. Another is that it can be used to study the retardant mechanism in the gas phase when TGA, DTA, or DSC cannot be used (because they only measure properties in the solid phase).

Table 6.7 shows the effect of inorganic additives on oxygen index and the yield of levoglucosan (Fung et al. 1972). Phosphoric acid is the most effective treatment of wood to increase the oxygen index and decrease the formation of levoglucosan. Ammonium dihydrogen orthophosphate, zinc chloride, and sodium borate are also very effective in reducing the yield of levoglucosan.

TABLE 6.6
Flame Spread Index for Different Woods Using the 25-Foot Tunnel Test

Species	Flame Spread Index
Douglas-fir	70–100
Western hemlock	60–75
Lodgepole pine	93
Western red cedar	70
Redwood	70
Sitka spruce	74–100
Yellow birch	105–110
Cottonwood	115
Maple	104
Red oak	100
Walnut	130–140
Yellow poplar	170–185

6.3.5 OTHER TESTS

Other tests that can be run on wood and fire-retardant–treated wood can determine smoke production, toxicity of smoke, and rate of heat release (ASTM 2002). The production of smoke can be a critical problem with some types of fire retardants. The 25-foot tunnel test uses a photoelectric cell to measure the density of smoke evolved. The effect of fire retardants on smoke production varies depending on the chemical used. Chemicals such as zinc chloride and ammonium phosphate generate much larger amounts of smoke as compared to borates. The toxicity of the smoke is also a critical consideration for fire-retardant–treated wood. A large percentage of fire victims are not touched by flames but are overcome from exposure to toxic smoke (Kaplan et al. 1982). The heat of combustion of wood varies depending on the species, resin content, moisture content, and other factors. The contribution to fire exposure depends on these factors along with the fire exposure and degree of combustion. Although the heat of combustion of wood does not change, fire retardants reduce the rate of heat release and extend the time at which the heat release begins to be measurable.

TABLE 6.7
Effect of Inorganic Additives on Oxygen Index and Levoglucosan Yield

Chemical	Oxygen Index (%)	Levoglucosan Yield (%)
Untreated	17.3	10.1
Potassium dihydrogen phosphate	18.5	0.9
Potassium hydrogen phosphate	18.6	0.2
Sodium borate	19.3	<0.1
Zinc chloride	19.6	0.3
Ammonium dihydrogen orthophosphate	19.6	0.8
Phosphoric acid	20.5	<0.1

Source: Fung 1972.

6.4 FIRE RETARDANTS

Fire-retardant treatments for wood can be classified into one of six classes: chemicals that promote the formation of increased char at a lower temperature than untreated wood degrades, chemicals which act as free-radical traps in the flame, chemicals used to form a coating on the wood surface, chemicals that increase the thermal conductivity of wood, chemicals that dilute the combustible gases coming from the wood with non-combustible gasses, and chemicals that reduce the heat content of the volatile gases.

In most cases, a given fire retardant operates by several of these mechanisms and much research has been done to determine the magnitude and role of each of these mechanisms in fire retardancy.

6.4.1 Chemicals that Promote the Formation of Increased Char at a Lower Temperature than Untreated Wood Degrades

Most of the evidence relating to the mechanism of fire retardancy in the burning of wood indicates that retardants alter fuel production by increasing the amount of char, reducing the amount of volatile, combustible vapors, and decreasing the temperature where pyrolysis begins. Figure 6.8 shows a TGA of untreated wood along with wood that has been treated with several inorganic fire retardants. Fire-retardant chemicals such as ammonium dihydrogen orthophosphate greatly increase the amount of residual char and lower the initial temperature of thermal decomposition. The amount of noncondensable gases increases at the expense of the flammable tar fraction. The chemical mechanism for the reduction of the combustible volatiles involves not only the ability of the fire retardant to inhibit the formation of levoglucosan (see the earlier discussion) and to catalyze dehydration of the cellulose to more char and fewer volatiles, but also its potential to enhance the condensation of the char to form cross-linked and thermally stable polycyclic aromatic structures (Shafizadeh 1984). Nanassy (1978) showed that Douglas-fir treated with either sodium chloride or ammonium dihydrogen orthophosphate increased both the char yield and the aromatic carbon content of the char (Table 6.8).

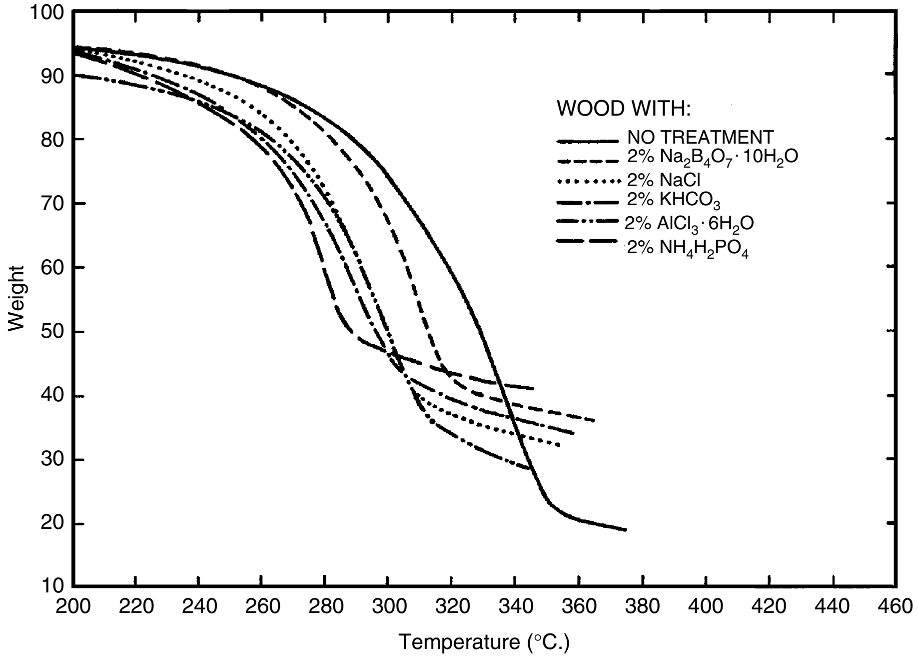

FIGURE 6.8 Thermogravimetric analysis of wood treated with various inorganic additives.

TABLE 6.8
Effect of Inorganic Additives on Char Yield and Aromatic Carbon Content of the Char

Chemical	Char Yield (wt%)	Aromatic Carbon in Char (wt%)
Untreated	15.3	13.7
Sodium chloride	17.5	16.8
Ammonium dihydrogen orthophosphate	28.9	18.6

Sources: Schafizadeh, 1984 and Nanassy, 1978.

Figure 6.9 shows the TGA of untreated cellulose along with cellulose that has been treated with several inorganic fire retardants. The thermal decomposition pattern for cellulose is similar to whole wood, except that pure cellulose is more thermally stable with the hemicelluloses removed.

All inorganic fire retardants reduce the amount of levoglucosan, regardless of the relative effectiveness of the fire retardant. This includes the effect of acidic, neutral, and basic additives on the levoglusosan yield. The acid treatment has the most pronounced effect on the reduction in the formation of levoglucosan.

During the heating of cellulose treated with either borax or ammonium dihydrogen orthophosphate, the degree of polymerization (DP) of the cellulose decreased (Fung et al. 1972). The DP decreased from 1110 to 650 after only two minutes of heating at 150°C with wood treated with ammonium dihydrogen orthophosphate. The DP dropped from 1300 to 700 after one hour of heating borax treated wood at 150°C. Both of these chemical treatments suppressed the formation of levoglucosan (see Table 6.7).

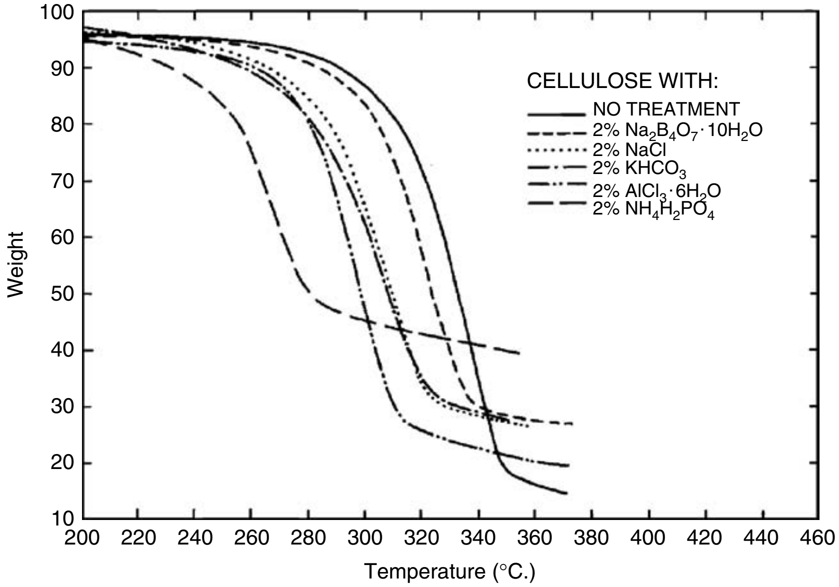

FIGURE 6.9 Thermogravimetric analysis of cellulose treated with various inorganic additives.

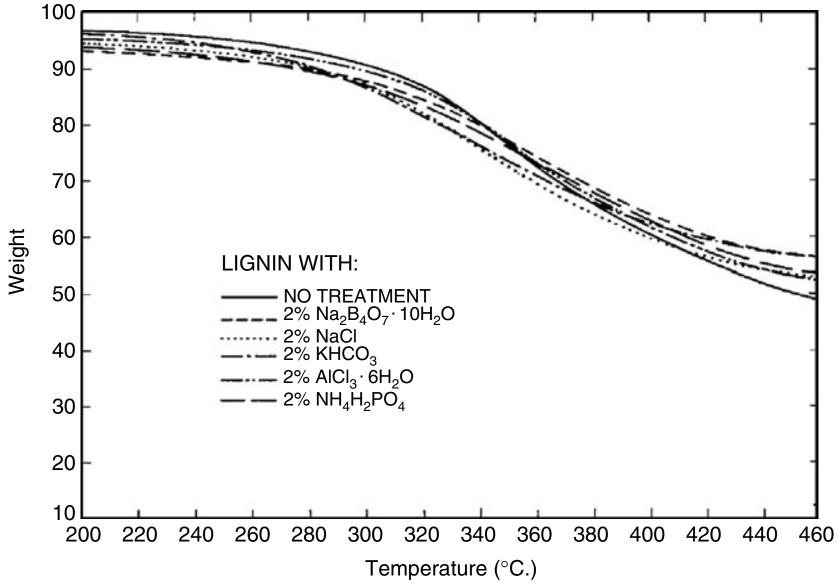

FIGURE 6.10 Thermogravimetric analysis of lignin treated with various inorganic additives.

Figure 6.10 shows the TGA of untreated lignin along with lignin that has been treated with several inorganic fire retardants. Treating lignin with the fire retardants has very little effect on the thermal decomposition of lignin.

6.4.2 CHEMICALS WHICH ACT AS FREE RADICAL TRAPS IN THE FLAME

Certain fire retardants affect vapor-phase reactions by inhibiting the chain reactions as shown below. Halogens such as bromine and chlorine are good free radical inhibitors and have been studied extensively in the plastics industry. Generally, high concentrations of halogen are required (15–30% by weight) to attain a practical degree of fire retardancy. The efficiency of the halogen decreases in the order Br > Cl > F. A mechanism for the inhibition of the chain branching reactions using HBr as the halogen is:

$$\mathrm{H\cdot + HBr \rightarrow H_2 + Br\cdot}$$

$$\mathrm{OH\cdot + HBr \rightarrow H_2O + Br\cdot}$$

The hydrogen halide consumed in these reactions is regenerated to continue the inhibition.

An alternate mechanism has been suggested for halogen inhibition that involves recombination of oxygen atoms (Creitz 1970):

$$\mathrm{O\cdot + Br_2 \rightarrow BrO\cdot + Br\cdot}$$

$$\mathrm{O\cdot + OBr\cdot \rightarrow Br\cdot + O_2}$$

Thus, the inhibitive effect results from the removal of active oxygen atoms from the vapor phase. Additional inhibition can result from removal of OH radicals in the chain-branching reactions:

$$\mathrm{BrO\cdot + \cdot OH \rightarrow HBr + O_2}$$

$$\mathrm{BrO\cdot + \cdot OH \rightarrow Br\cdot + HO_2}$$

Some phosphorus compounds have also been found to inhibit flaming combustion by this mechanism.

6.4.3 Chemicals Used to Form a Coating on the Wood Surface

A physical barrier can retard both smoldering and flaming combustion by preventing the flammable products from escaping and preventing oxygen from reaching the substrate. These barriers also insulate the combustible substrate from high temperatures. Common barriers include sodium silicates and coatings that intumesce (release a gas at a certain temperature that is trapped in the polymer coating the surface). *Intumescent systems* swell and char on exposure to fire to form a carbonaceous foam. They consist of several components, including a char-producing compound, a blowing agent, a Lewis-acid dehydrating agent, and other chemical components.

In the intumescent systems, the char-producing compound, such as a polyol, will normally burn to produce CO_2 and water vapor and leave flammable tars as residues. However, the compound can esterify when it reacts with certain inorganic acids, usually phosphoric acid. The acid acts as a dehydrating agent and leads to increased yield of char and reduced volatiles. Such char is produced at a lower temperature than the charring temperature of the wood. Blowing agents decompose at determined temperatures and release gases that expand the char. Common blowing agents include dicyandiamide, melamine, urea, and guanidine; they are selected on the basis of their decomposition temperatures. Many blowing agents also act as a dehydrating agent. Other chemicals can be added to the formulation to increase the toughness of the surface foam.

6.4.4 Chemicals that Increase the Thermal Conductivity of Wood

A metal alloy with a melting point of 105°C can be used to treat wood. Upon heating, the temperature rise in the metal-alloy–treated wood is slower than non-treated wood until the melt temperature is reached (Browne 1958). Above the melt temperature of the metal alloy, the rise in temperature is the same for treated and non-treated wood.

Another thermal theory suggests that fire retardants cause chemical and physical changes so that heat is absorbed by the chemical to prevent the wood surface from igniting. This theory is based on chemicals that contain a lot of water of crystallization. Water will absorb latent heat of vaporization from the pyrolysis reactions until all of the water is vaporized. This serves to remove heat from the pyrolysis zone, thereby slowing down the pyrolysis reactions. This is why wet wood burns more slowly than dry wood. Once the water is removed, the wood undergoes pyrolysis independent of the past moisture content of the wood.

6.4.5 Chemicals that Dilute the Combustible Gases Coming from the Wood with Non-Combustible Gases

Chemicals such as dicyandiamide and urea release large amounts of non-combustible gases at temperatures below the temperature at which the major pyrolysis chemistries start. Chemicals such as borax release large amounts of water vapor. Any reduction in the percentage of flammable gases would be beneficial because it increases the volume of combustible volatiles needed for ignition. Also, the movement of gases away from the wood may dilute the amount of oxygen near the boundary layer between the wood and the vapor-phase reaction.

6.4.6 Chemicals that Reduce the Heat Content of the Volatile Gases

As previously seen in Section 4.1, the addition of inorganic additives lowers the temperature at which active pyrolysis begins, and this resulting decomposition leads to increased amounts of char and reduced amounts of volatiles. This is due to the increased dehydration reactions, mainly in the cellulose component of wood. However, other competing reactions also occur, such as decarbonylation, decomposition of simpler compounds, and condensation reactions. All of these reactions compete with each other. As a result, shifts favoring one reaction over another also change the overall heat of reaction. Differential thermal analysis is used to determine these changes in heats of reactions and can help gain an understanding about these competing reactions.

DTA of wood in helium shows two endothermic reactions followed by a smaller exothermic one. The first endothermic reaction, which peaks around 125°C, is a result of evaporation of water and desorption of gases; the second, peaking between 200–325°C, indicates depolymerization and volatilization. At around 375°C these endothermic reactions are replaced with a small exothermic peak. When the wood sample is run in oxygen, these endothermic peaks are replaced by strong exothermic reactions. The first exotherm, around 310°C for wood and 335°C for cellulose, is attributed to the flaming of volatile products; the second exotherm, at 440°C for wood and 445°C for both cellulose and lignin, is attributed to glowing combustion of the residual char.

DTA of inorganic fire-retardant–treated wood in oxygen shifts the peak position temperatures and/or the amount of heat released. Sodium tetraborate, for example, reduces the volatile products exotherm considerably, increases the glowing exotherm, and shows a second glowing peak around 510°C. Sodium chloride also reduces the first exotherm and increases the size of the second, but does not produce a second glowing exotherm as did the sodium tetraborate. Wood treated with ammonium phosphate is the most effective in both reducing the amount of volatile products and also reducing the temperature where these products are formed. Ammonium phosphate almost eliminates the glowing exotherm.

Fire retardant treatments of this type reduce the average heat of combustion for the volatile pyrolysis products released at the early stage of pyrolysis below the value associated with untreated wood at comparable stages of volatilization. At 40% volatilization, untreated wood has a 29% release of volatile products' heat of combustion; treated wood has only released 10–19% of this total heat. Of all the chemicals tested, only sodium chloride, which is known to be an ineffective fire retardant, does not reduce the heat content.

6.4.7 Phosphorus-Nitrogen Synergism Theories

One role phosphoric acid and phosphate compounds play in the fire retardancy of wood is to catalyze the dehydration reaction to produce more char. This reaction pathway is just one of several that are taking place all at once, including decarboxylation, condensation, and decomposition. The effectiveness of fire retardants containing both phosphorus and nitrogen is greater than the effectiveness of each of them by themselves.

The interaction of phosphorus and nitrogen compounds produces a more effective catalyst for the dehydration because the combination leads to further increases in the char formation and greater phosphorus retention in the char (Hendrix and Drake 1972). This may be the result of increased cross-linking of the cellulose during pyrolysis through ester formation with the dehydrating agents. The presence of amino groups results in retention of the phosphorus as a nonvolatile amino salt, in contrast to some phosphorus compounds that may decompose thermally and be released into the volatile phase. It is also possible that the nitrogen compounds promote polycondensation of phosphoric acid to polyphosphoric acid. Polyphosphoric acid may also serve as a thermal and oxygen barrier because it forms a viscous fluid coating.

6.4.8 Fire-Retardant Formulations

Many chemicals have been evaluated for their effectiveness as fire retardants. The major fire retardants used today include chemicals containing phosphorus, nitrogen, boron, and a few others. Most fire-retardant formulations are water leachable and corrosive, so research continues to find more leach-resistant and less corrosive formulations.

TABLE 6.9
Effects of Inorganic Additives on Thermogravimetric Analysis

Additive	Percent Weight Loss at 500°C
Phosphoric acid	61
Ammonium dihydrogen orthophosphate	66
Zinc chloride	74
Sodium hydroxyde	79
Boric acid	81
Sodium chloride	82
Tin chloride	84
Diammonium sulfate	86
Sodium tetraborate decahydrate	89
Sodium phosphate	91
Ammonium chloride	93
Untreated wood	93

6.4.8.1 Phosphorus

Chemicals containing phosphorus are one of the oldest classes of fire retardants. Monoammonium and diammonium phosphates are used with nitrogen compounds, since the synergistic effect allows for less chemical to be used (Hendrix and Drake 1972, Langley et al. 1980, Kaur et al. 1986). Organophosphorus and polyphosphate compounds are also used as fire retardants. Ammonium polyphosphate at loading levels of 96 kg/m^3 gives a flame-spread index of 15 according to ASTM E84 (Holmes 1977). This treatment generates a low smoke yield but it is corrosive to aluminum and mild steel. Other formulations containing phosphorus are mixture of guanyl urea phosphate and boric acid, and phosphoric acid, boric acid, and ammonia. Table 6.9 shows the effectiveness of some of the fire retardants in terms of the percent of weight loss at 500°C. The most effective chemical is phosphoric acid, with a weight loss of 61% as compared to 93% weight loss for untreated wood.

6.4.8.2 Boron

Borax (sodium tetraborate decahydrate) and boric acid are the most often used fire retardants. The borates have low melting points and form glassy films on exposure to high temperatures. Borax inhibits surface flame spread but also promotes smoldering and glowing. Boric acid reduces smoldering and glowing combustion but has little effect on flame spread. Because of this, borax and boric acid are usually used together. The alkaline borates also result in less strength loss in the treated wood and is less corrosive and hydroscopic (Middleton et al. 1965). Boron compounds are also combined with other chemicals such as phosphorus and amine compounds to increase their effectiveness. Table 6.9 shows that wood treated with boric acid shows a weight loss of 81% and borax an 89% weight loss at 500°C, which is not as effective as phosphorus compounds.

6.4.9 LEACH RESISTANT FIRE-RETARDANTS

A fire-retardant treatment that is resistant to water leaching is a requirement in some building codes today. Fires have spread from home to home due to wood shake roofs, and some states now require wood-based roofing materials to be treated with a leach-resistant fire retardant.

The most widely studied leach-resistant fire retardant system is based on amino-resins (Goldstein and Dreher 1964). Basically, the resin system consists of a combination of a nitrogen source (urea, melamine, guanidine, or dicyandiamide) with formaldehyde to produce a methylolated amine.

The product is then reacted with a phosphorus compound such as phosphoric acid. Other formulations include mixtures of dicyandiamide, melamine, formaldehyde, and phosphoric acid, or dicyandiamide, urea, formaldehyde, phosphoric acid, formic acid, and sodium hydroxide. Leach resistance is attributed to polymerization of the components within the wood (Goldstein and Dreher 1961). Another formulation uses a urea and melamine amino-resin (Juneja and Fung 1974). The stability of these resins is controlled by the rate of methylolation of the urea, melamine and dicyandiamide. The optimum mole ratio for stability of these solutions is 1:3:12:4 for urea ormelamine, dicyandiamide, formaldehyde, and orthophosphoric acid. Lee et al. (2004) bonded phosphoramides to wood by reacting phosphorus pentoxide with amines *in situ*. Leach resistance was greatly improved and the mechanism of effectiveness was said to be due to an increase in the dehydration mechanism.

Wood has been reacted with fire-retardant chemicals such as phosphorus pentoxideamine complexes (Lee et al. 2004) or glucose diammonium phosphate (Chen 2002) that results in treatments that are leach resistant (Rowell et al. 1984) (see Chapter 14, Section 5.10).

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