6 Thermal Properties, Combustion, and Fire Retardancy of Wood

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One of the greatest assets of cellulosic resources is their compatibility with nature, including their combustibility and degradability which allow for constant turnover and regeneration of these natural resources. A fundamental understanding of these properties and possible methods for controlling them is essential for protection and better utilization of these resources.

Combustion of wood involves a complex series of physical transformations and chemical reactions that are further complicated by the heterogeneity of the substrate. Wood, and cellulosic materials do not burn directly but under the influence of sufficiently strong heat sources they decompose to a mixture of volatiles, tarry compounds, and highly reactive carbonaceous char (Shafizadeh

1984) (Figure 6.1). Gas phase oxidation of the combustible volatiles and tarry products produces flaming combustion. Solid-phase oxidation of the remaining char produces glowing or smoldering combustion, depending on the rate of oxidation.

Lignocellulosic materials decompose on heating and when exposed to an ignition source by two different mechanisms. The first, which is dominated at temperatures below 300°C, involves the degradation of the polymers by breaking internal chemical bonds, dehydration (elimination of water), formation of free radicals, carbonyl, carboxyl and hydroperoxide groups, formation of carbon monoxide (CO) and carbon dioxide (CO_2), 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, formation of intermediate products such as anhydromonosaccharides which is converted into low molecular weight products, oligosaccharides and polysaccharides which leads to

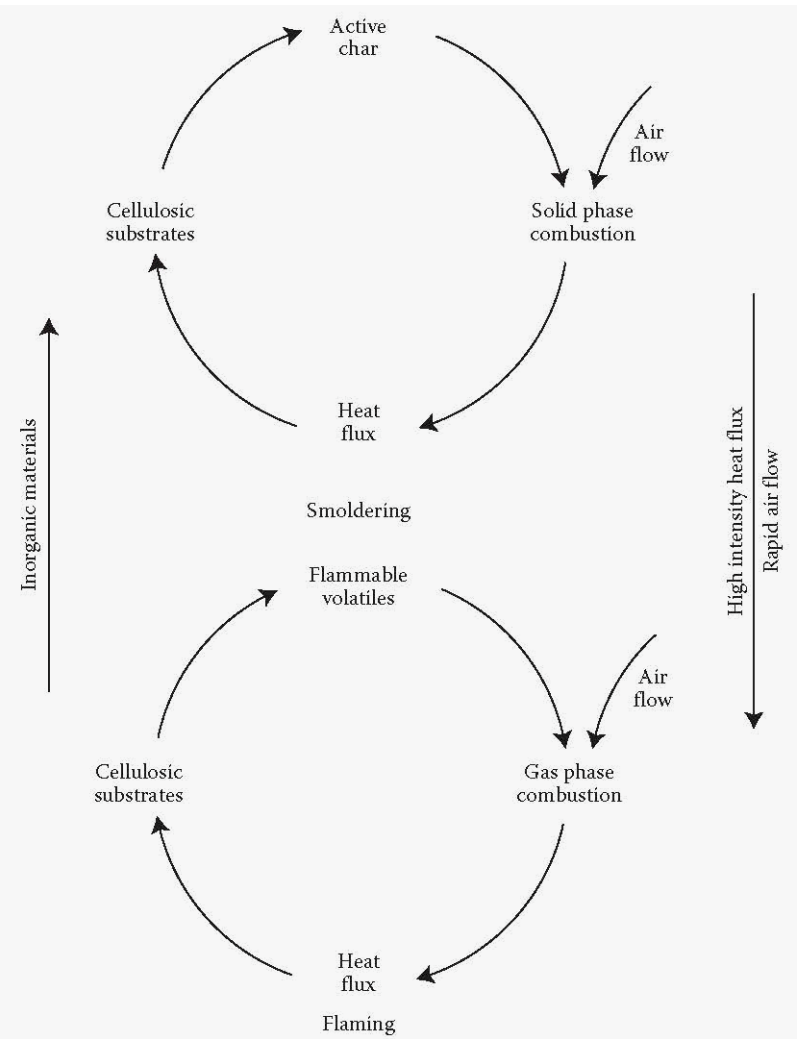

FIGURE 6.1 Graphic presentation of the flaming and smoldering combustion showing the respective roles of combustible volatiles and active char produced by pyrolysis under heat flux at different conditions.

carbonized products (Kawamoto et al. 2003) and high volatile production rates at a high enough heating value to be easily ignitable with air.

6.1 PYROLYSIS AND COMBUSTION

The simplest method of evaluating the thermal property of degradation for wood is by thermogravimetric analysis (TGA). Figure 6.2 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 weight loss is measured as function of temperature. The temperature is usually raised to 500–600°C in nitrogen at a few °C per minute. The temperature can then be lowered to around 300°C, oxygen is introduced into the system, and the temperature increased again. This second scan will show the combustion of the char in oxygen.

A simple thermogram run in nitrogen is shown in Figure 6.3 for pine (Shafizadeh 1984). As wood is heated from room temperature to 100°C, very little chemical reactions take place. At approximately 100°C, any moisture in the wood is vaporized out. As the wood increases in temperature, very little degradation occur until about 200°C when chemical bonds start to break via dehydration and, possibly, free radical mechanisms to eliminate water and producing volatile gasses. In the absence of, or in limited amounts of oxygen, this thermal degradation process is called pyrolysis. The volatile gasses produced diffuse out of the wood into the surrounding atmosphere. Figure 6.4 shows the first derivative of the TGA curve for pine.

Whole wood starts to thermally degrade at about 250°C according to this TGA (see Figure 6.5). With more sensitive TGA coupled with evolved gas analysis, one can detect volatile organic compounds (VOCs) beginning around 130°C, the terpene-related extractives starting around 200°C (McGraw and others 1999), and the water vapor and CO, from dehydration and decarboxylation

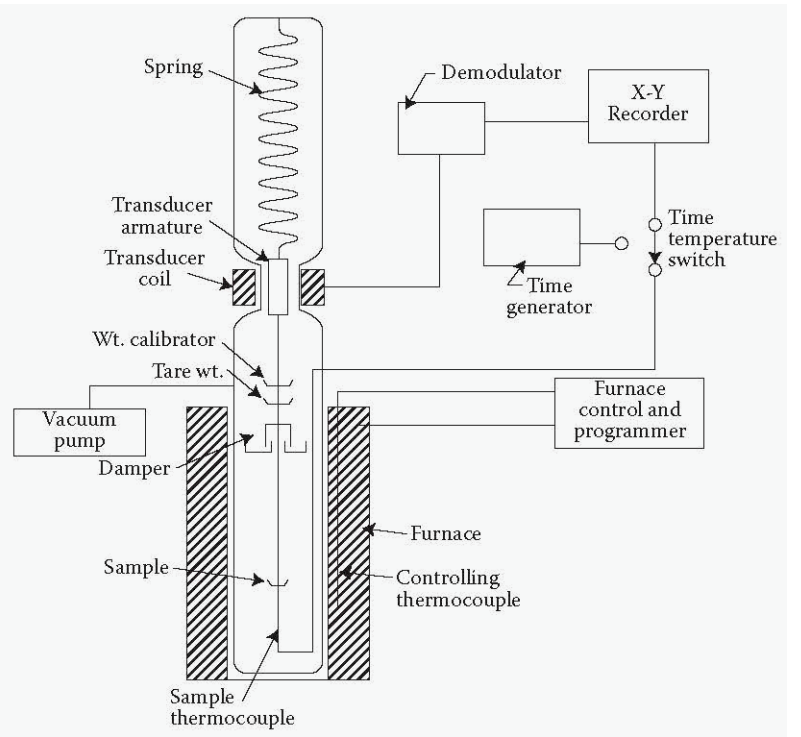

FIGURE 6.2 Schematic diagram of a simple thermogravimetric analysis system

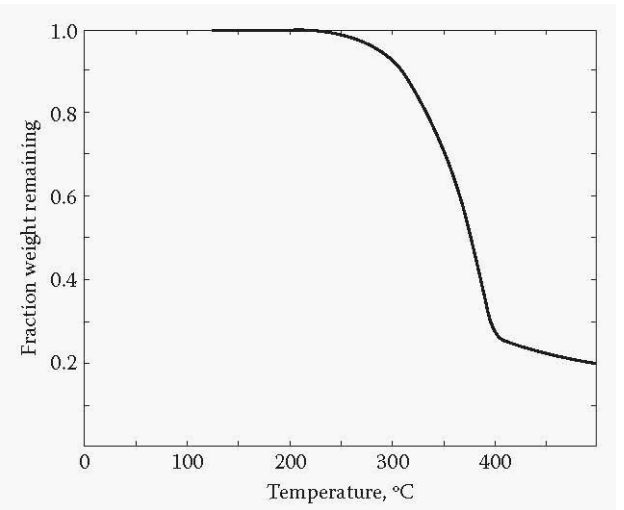

FIGURE 6.3 Thermogravimetric analysis ofpine.

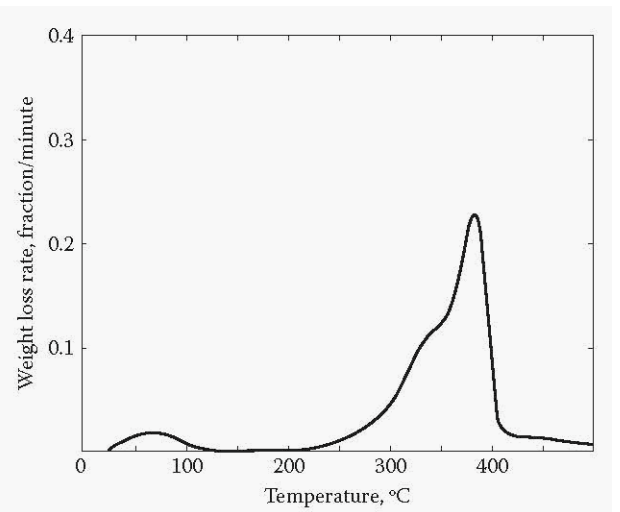

FIGURE 6.4 Derivative thermogravimetric analysis ofpine.

processes that can reduce carbohydrate polymers very slowly to a mostly carbon residue within these temperatures (Funke and Ziegler 2010). Between about 300°C and 375°C, the majority of the carbohydrate polymers have degraded into combustible volatiles and only lignin remains as being largely not degraded. 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 when it decomposes rapidly and 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 is shown in Table 6.1 (Shafizadeh 1983). Note the tar at 28% mass content has many higher molecular weight compounds that can be resolved with modern gas chromatography–mass spectrometry (GC–MS) (www.TarWeb.net).

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

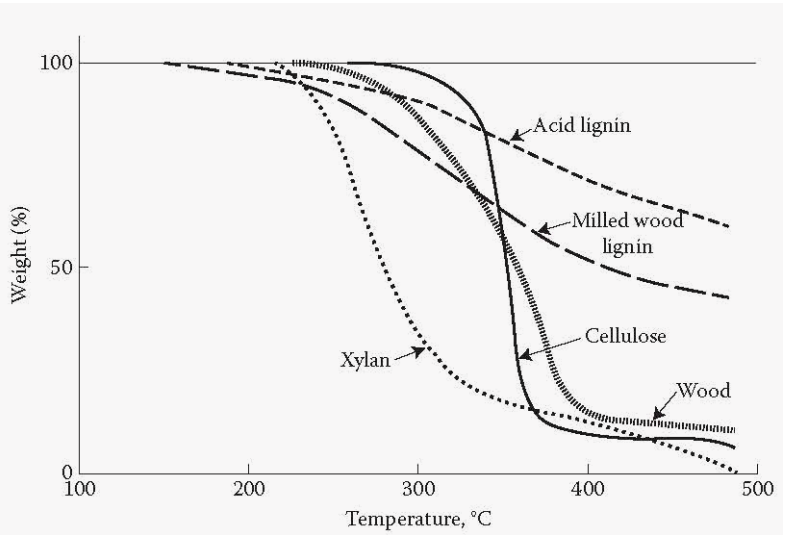

FIGURE 6.5 Thermogravimetric analysis of cottonwood and its cell wall components,

TABLE 6.1
Pyrolysis Products of Wood

Product	Percent in Mixture
Acetaldehyde	2.3
Furan	1.6
Acetone propionaldehyde	1.5
Propenal	3.2
Methanol	2.1
2,3-Butanedione	2.0
l-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

volatile gasses while lignin decomposition leads mainly to tars and char. Figure 6.6 shows the pyrolysis and combustion of cellulose (Shafizadeh 1983). 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. The formation of CO and CO_2 are much faster in oxygen than in nitrogen and this rate accelerates as the temperature increases. Table 6.2 shows the rate constants for the depolymerization of cellulose in air and nitrogen (Shafizadeh 1983) for very slow pyrolysis at the lowest temperatures using the simplest mechanistic kinetics equation. These rate constants and mechanistic kinetics equations are

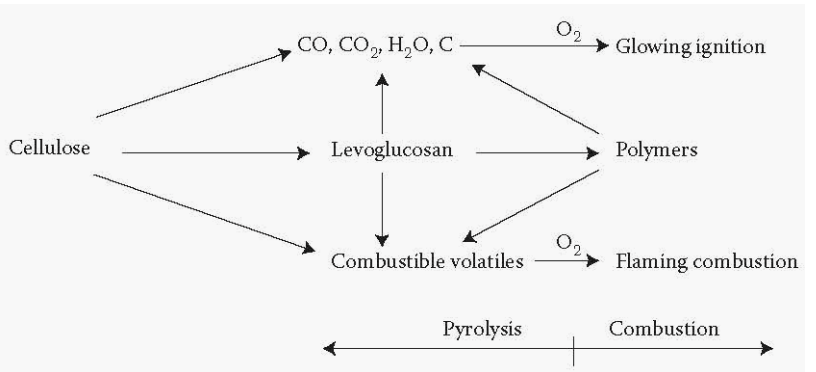

FIGURE 6.6 Pyrolysis and combustion of cellulose

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)[a]
150	N_2	1.1
	Air	6.0
160	N_2	2.8
	Air	8.1
170	N_2	4.4
	Air	15.0
18	N_2	9.8
	Air	29.8
190	N_2	17.0
	Air	48.9

[a] One mol of glucose.

continually being updated, particularly due to the fairly recent surge in biomass energy research using slow and fast pyrolysis.

Cellulose while degrading also produces combustible volatiles such as acetaldehyde, propenal, methanol, butanedione, and acetic acid. When the combustible volatiles mix with oxygen and are then heated to the ignition temperature, exothermic combustion occurs. The heat from these reactions in the vapor phase transfer heat back into the wood increasing the rate of pyrolysis in the solid phase via increasing the solid temperature to a higher level. 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 primary products such as anhydromonosaccharides including levoglucosan (1,6-anhydro-ß-D-glucopyranose) and 1,6-anhydro-ß-D-glucofuranose which is converted into low molecular weight products, randomly linked oligosaccharides and polysaccharides which leads to carbonized products (Figure 6.7).

Figure 6.8 shows the formation of levoglucosan from cellulose. A single unit of cellulose, glucose, undergoes dehydration to form levoglucosan, levoglucosenone, and 1,4:3,6-dianhydro-α-D-glucopyranose. Other products are also known to form such as the 1,2-anhydride and the 1,4-anhydride, 3-deoxy-D-erythrohexosulose, 5-hydroxymethyl-2-furaldehyde, 2-furaldehyde (furfural),

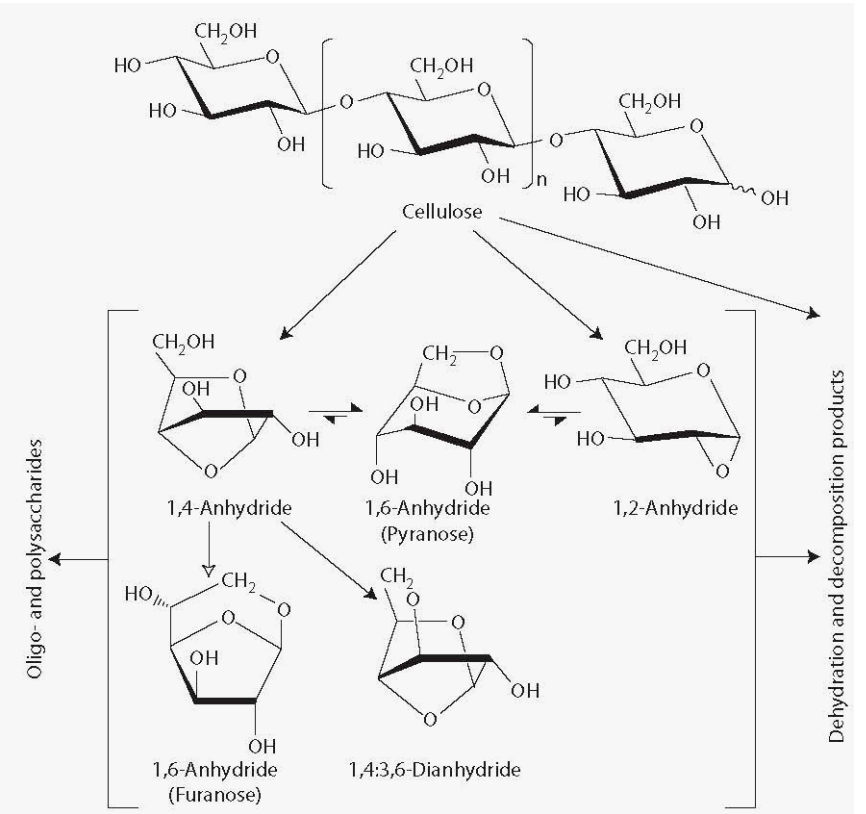

FIGURE 6.7 Pyrolysis of cellulose to anhydro sugars.

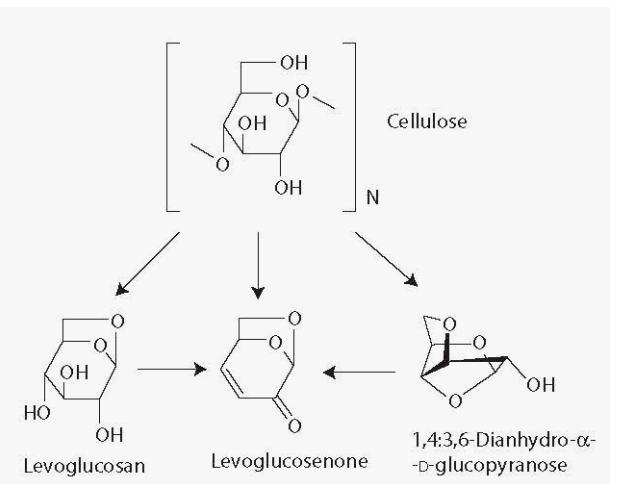

FIGURE 6.8 Formation of levoglucosan and other monomers from cellulose,

other furan derivatives, 1,5-anhydro-4-deoxy-D-hex-1-ene-3-ulose, and other pyran derivatives (Shafizadeh 1983). 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 **Q5** the gas phase (Shafizadeh 1982). The anhydromonosaccharides can recombine forming polymers

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

which can then degrade to CO, CO_2, water, and secondary char residues or to combustible volatiles.

Above 300°C, the tar-forming reactions increase in rate and the formation of primary char decreases. Table 6.3 shows the percent of char and tar products formed from cellulose as a function of temperature (Shafizadeh 1983). At 300°C, there is about 28% tar and 20% char products. As the temperature increases to 350°C, the tar products yield increases to 38% and the char to 8%. At 500°C, the tar products yield stays about the same but the char yield decreases to 2%. These occur at the lower pressures and low residence time, whereas at high pressures and higher residence time the cellulosic tar will degrade into secondary char and gasses in greater amounts (Mok and Antal 1983).

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 and by 400°C, the yield has decreased to 16.7%. The char yield for whole wood at 400°C is 24.9% and for isolated lignin, 73.3%. The carbon, hydrogen,

TABLE 6.4
Char Yield from Cellulose, Wood and Lignin, and Chemical Composition of the Char[a]

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

[a] Isothermal pyrolysis, 5 min at temperature.

and oxygen analysis for the various char yields shows 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 1983). Lignin mainly contributes to primary char formation and cellulose and the hemicelluloses mainly to volatile pyrolysis products that are responsible for flaming combustion.

The intensity of combustion can be expressed as:

$$I_R = \frac{-\Delta H \, dm}{dt}$$

where

I_R = reaction density (rate of heat release);
$-\Delta H$ = heat of combustion, and
dm/dt = rate mass of fuel loss

Table 6.5 shows the heat of combustion for cellulose, whole wood, bark, and lignin as determined from oxygen bomb calorimetry and their pyrolysis yields from a TGA. The highest levels of volatiles are produced by cellulose which has the lowest heat of combustion and the lowest percent char formation. The next level of volatiles is produced by whole wood with slightly higher heat of combustion and char yield as compared to cellulose. Bark has a higher heat of combustion as compared to wood, 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. We note that the heat of combustion value at oxygen bomb calorimetry conditions for the virgin material are generally less than the heat of combustion value for the developed char, and also higher than the heat of combustion of the developed volatiles for the corresponding material (Dietenberger 2002). Therefore assigning heat of combustion values to the fuel components during flaming or glowing combustion is not straightforward and requires a very detailed mechanistic kinetics theory.

The high rate of heat released upon flaming combustion provides sufficient energy to pyrolyze the remaining solid wood and thus propagate the fire. For wood, external heat sources in addition to flaming combustion or enhanced flaming with enriched oxygen is usually needed to sustain creeping flame spread (White and Dietenberger 1999, White 1979). 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 nonignitable 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

Virgin Fuel	Heat of Combustion ΔH 25°C (cal/g)	Char Yield (%)[a]	Combustible Volatiles (%)[a]
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

[a] Heating rate 200 C/min to 400°C and held for 10 min.

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 and this layer is an insulation barrier protecting the wood below the burning layer (self-insulating). The comparative fire resistance of wood and metal was never more graphically shown than the pictures taken after many hours of burning in the 1953 fire at a casein plant in Frankfort, New York (Figure 6.9). The steel girders softened and failed at high temperature and fell across the 12 by 16 inch laminated wood beams that were charred but still strong enough to hold the steel girders. This charring protecting property of structural wood has found many applications, such as railroad wooden bridges.

To reduce the flammability 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 12 stories high starting in 1899 (Eickner 1966).

Standards that pertain to fire safety in structures are specified in building codes and fire codes (White and Dietenberger 1999). 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 that imply large-scale test performances to obtain the required ratings. However, when developing improved fire-retardant treatments (FRT) it is advantageous to use laboratory scale tests that give an indication of improved fire retardancy of wood-based products. The promising FRTs that pass these initial tests can then be applied to the relatively more expensive large-scale tests to achieve the required rating.

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. 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. 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. This is referred to as derivative thermogravimetry (Slade and Jenkins 1966) with results shown in Figure 6.4 for pine.

FIGURE 6.9 Wood beam survives fire in casein plant in Frankfort, NY.

6.3.2 Differential Thermal Analysis (DTA) and Differential Scanning Calorimeter (DSC)

DTA measures the amount of heat liberated or absorbed by a wood sample as it moves from one physical transitions state to another (i.e., melting, 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, to provide kinetic data, and to 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 at the same as the reference.

6.3.3 Cone Calorimeter

A cone calorimeter (Figure 6.10) is a modern instrument used to study the fire behavior of small samples of various materials in condensed phase. It is widely used in the field of Fire Safety Engineering. It gathers data regarding the ignition time, mass loss rate (MLR), combustion products, heat release rate (HRR), and other parameters as a function of time associated with the finitely thick material's burning properties. A sample is mounted on a load cell that will measure mass loss during a test. The fuel sample can be exposed to different heat fluxes from the cone heater over its 10 by 10 cm surface, typically set at 50 kW/m^2 to simulate the ignition burner heat fluxes in large-scale regulatory tests. The principle for the measurement of the heat release rate is based on the Huggett's

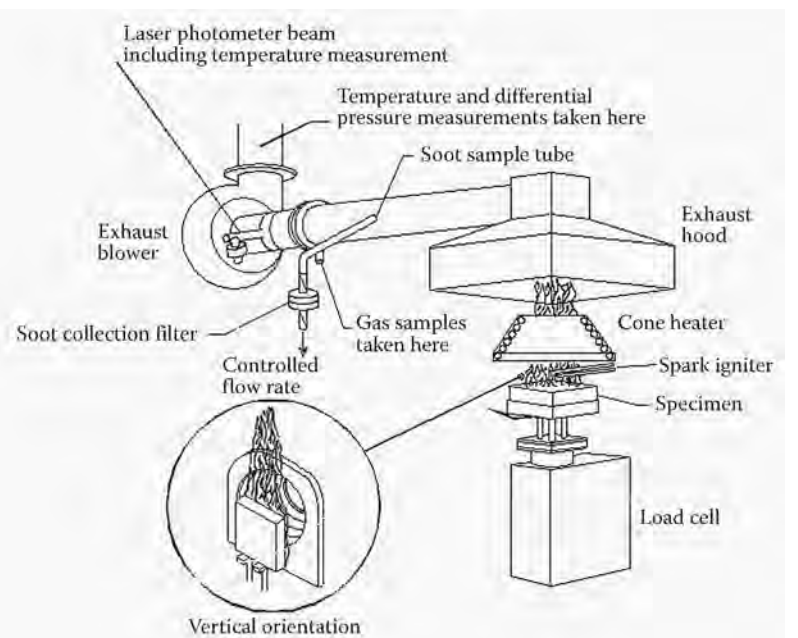

FIGURE 6.10 Schematic diagram of a cone calorimeter.

principle that the net heat of combustion of any organic material is directly related to the amount of oxygen required for combustion (Huggett 1980), which was strongly reaffirmed for wood volatiles and char (Dietenberger 2002). The cone calorimeter produces large amounts of data including curves of heat release, smoke, and mass loss, CO, CO_2, and other gas yields. These data are automatically collected by the software used with the calorimeters. The ASTM International Standard is ASTM E1354-11a, "Standard Test Method for Heat and Visible Smoke Release Rates for Materials and Products using an Oxygen Consumption Calorimeter." (www.astm.org/Standards/E1354.htm)If only the mass loss measurement under fire conditions is needed to compare fire retardancy of materials, one can use the lower cost mass loss calorimeter, ASTM E2102 or the fire tube, ASTM E69.

6.3.3.1 Cone Calorimeter Tests on Wood

Three distinct uses of the cone calorimeter data, particularly for fire retardancy, have been developed to (1) compare the fire response of materials to assess their fire performance, for materials development, or pyrolysis and burning model developments, (2) derive the material parameters needed as input into mathematical models for the full-/scale room room/corner test assessment, and (3) determine for regulatory purposes the characteristic parameters such as peak HRR or total heat evolved (Schartel and Hull 2007). In the first main use, FRT results in delayed ignition, reduced heat release rate, reduced smoke production rate, and slower spread of flames. HRRs are markedly reduced by FRT (Figure 6.11). Note that the reduction in HRR (and MLR) after the initial peak HRR (PHRR) shortly after ignition is due to the insulating char development in conjunction with thermal wave traveling through the thick material resulting in the pyrolysis front slowing down, while the second peak HRR is due to combined effects of thermal wave termination at the insulated back surface and appearance of glowing combustion (Hagge et al. 2004). The transition from flaming to glowing is evidenced by an almost doubling of the effective heat of combustion (EHC = HRR/MLR) as the combustion transitions from volatiles to char oxidations. Flame-retardant treatment of wood generally improves the fire performance by reducing the amount of flammable volatiles released during fire exposure or by reducing the effective heat of combustion, or both. Both results have the effect of reducing the HRR, particularly during the initial stages of fire, and thus consequently reducing the rate of flame spread over the surface (Dietenberger and 2001). The wood fire may then self-extinguish when the primary heat source is removed.

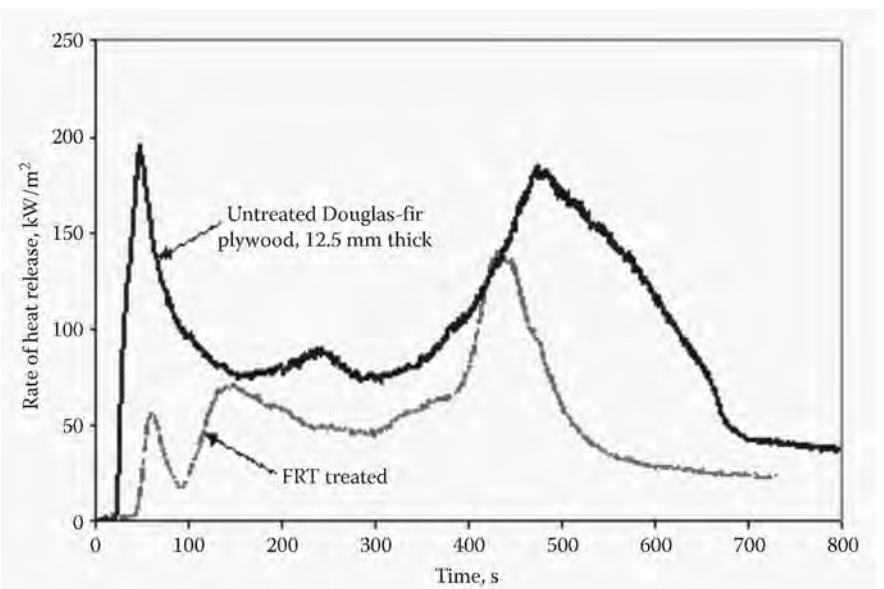

FIGURE 6.11 Heat release curves for untreated and FRT-treated Douglas-fir plywood, 12.5 mm thick.

TABLE 6.6
Comparison of Room/Corner Flashover Times and the Cone's Global Parameters

Material	TFO [s] at 20 kW/m²	TFO [s] predict	Thick mm	Tig [s]	PHRR kW/m²	THR MJ/m²	peakSEA m²/s
Wafer board	141	143	13	21.4	208	101	145
OSB	186	211	11.5	23.3	204	91	119
Hardboard	222	299	7	27.6	189	93	119
Particleboard	237	183	12.8	31.4	211	102	136
Southern pine board	240	241	19	21.4	181	143	323
Southern pine plywood	321	274	11	19.1	197	65	126
Douglas-fir plywood ASTM	474	513	11.8	17.6	173	67	81
Redwood lumber	498	465	19	18.9	171	95	200
Douglas-fir plywood	531	528	12	16.6	168	74	97
White spruce lumber	594	559	17.3	17.0	165	89	122
FRT rigid PU foam	621	631	23	2.69	89.9	4.0	1061
FRT Douglas-fir plywood	849	869	12.5	34.2	72	34	10
FRT Southern pine plywood	882[a]	860	11.3	62.5	88	39	75
Type-X gypsum board	NFO	NFO	16	48	118	2.79	6

[a] 300 s added to measured TFO for burner profile glitch.

The global material parameters of the cone calorimeter data that are of significance to flame spread modeling via theoretical analytical solutions of fire growth are time to piloted ignition (TIG), peak HRR (PHRR), total HRR (THRR), and smoke extinction area (SEA), obtained with a horizontal sample exposed to irradiance of 50 kW/m² (Dietenberger and White 2001). These are listed in Table 6.6 for various panel products that span the wide range of flammability ratings and are arranged from the most flammable (waferboard) to the least flammable material (Type-X gypsum board) according to ASTM E84 results (discussed in next section). The flammability ratings for the full-scale room/corner tests (ISO 9705) with the 1001300 kW pilot burner in the corner of wall-only mounted panels is based on time-to-flashover (TFO) measured in various ways, the most objective measure is the occurrence of 20 kW/m² on the floor center. None of the cone's global parameters by themselves give any indication of the room's flammability ratings, not until we utilize the complex exponential root terms of the theoretical upward fire spread model that defines the flame spreading into accelerating, neutral, or damping fire spread modes in a simple empirical relationship (Dietenberger and White 2001) for various full-scale tests. It was interesting that the similar analysis can be applied to plastics with and without FRT, which is helpful in evaluating the wood–plastic composites also.

6.3.4 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 in North America, flame-spread ratings are determined by a 25 foot long tunnel test which is an approved standard test method (ASTM E 84, www.astm.org/Standards/E84.htm). 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. In the building codes, the classes for flame spread index are A (FSI of 0–25), B (FSI of 26–75), and C (FSI of 76–200). Generally, codes specify FSI for interior finish based on building occupancy, location within the building, and availability of automatic sprinkler protection. The more restrictive classes, Classes A and B, are generally prescribed for stairways and corridors

TABLE 6.7
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

that provide access to exits. In general, the more flammable classification (Class C) is permitted for the interior finish of other areas of the building that are not considered exit ways or where the area in question is protected by automatic sprinklers. In other areas, there are no flammability restrictions on the interior finish and unclassified materials (i.e., more than 200 FSI) can be used.

Two-foot tunnel test (ASTM D3806-98(2011), www.astm.org/Standards/D3806.htm) and 8-foot tunnel test (Peters and Eickner 1962) have also been used for research applications. All tunnel tests measure the surface flame spread of the wood although each differs in the method of the exposure and type of flame spreading. 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 is the most severe exposure where the specimen is exposed for 10 min to a high heat flux burner in an assisted air flow flame spread configuration. An extended test of 30 min is a requirement for FRT products (ASTM E2768-11, www.astm.org/Standards/E2768.htm). 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 tool for development work on fire retardants. Table 6.7 shows average values for the flame spread index of several wood species (White 1999). Extensive listing of wood materials is at American Wood Council website (http://awc.org/publications/DCA/DCAl/DCAl.pdf).

6.3.5 Critical Oxygen Index Test

The oxygen index test (ASTM D2863-10, www.astm.org/Standards/D2863.htm) measures the minimum concentration of oxygen in an oxygen–nitrogen mixture that will just support downward creeping flame spread of a test specimen. Highly flammable materials have low oxygen index, less flammable materials have high values (White 1979). One advantage of this test is that very small specimens can be used and it can be used to study the retardant mechanism in the dynamic flaming environment that cannot be done with TGA, DTA, or DSC because they only measure degradation and combustion properties in a quasi-steady environment far removed from real-world fires.

Table 6.8 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 6.8
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	<0.3
Zinc chloride	19.6	0.3
Ammonium dihydrogen orthophosphate	19.6	0.8
Phosphoric acid	20.5	<0.1

Source: Adapted from Fung, D.P.C., Tsuchiya, Y., and Sumi, K. 1972. *Wood Sci.* 5(1): 38–43.

6.3.6 Other Tests

Other tests that can be run on wood and fire retardant-treated wood determine smoke production, toxicity of smoke, and rate of heat release. 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. Chemicals such as zinc chloride and ammonium phosphate generate much larger amounts of smoke as compared to borates. The commercial FRT applied to plywood greatly reduces the smoke production in comparison to untreated plywood in cone calorimeter tests (Table 6.6). 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 as a result of exposure to toxic smoke (Kaplan et al. 1982). The heat of combustion of wood varies somewhat 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 overall heat of combustion of wood does not change, fire retardants reduce the rate of heat release by reducing volatization rate and volatile heat of combustion as well as reduce oxidation rates of the chars to dramatically reduce their contribution to unsafe or unwanted fires.

6.4 FIRE RETARDANTS

Fire retardant treatments for wood can be classified into one of six classes: (1) chemicals that promote the formation of increased char at a lower temperature than untreated wood degrades, (2) chemicals which act as free radical traps in the flame, (3) chemicals used to form a coating on the wood surface, (4) chemicals that increase the thermal conductivity of wood, (5) chemicals that dilute the combustible gasses coming from the wood with noncombustible gasses, and (6) chemicals that reduce the heat content of the volatile gasses (LeVan 1984). 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 Degradation

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 and reducing the amount of volatile, combustible vapors, and decrease the temperature where pyrolysis begins.

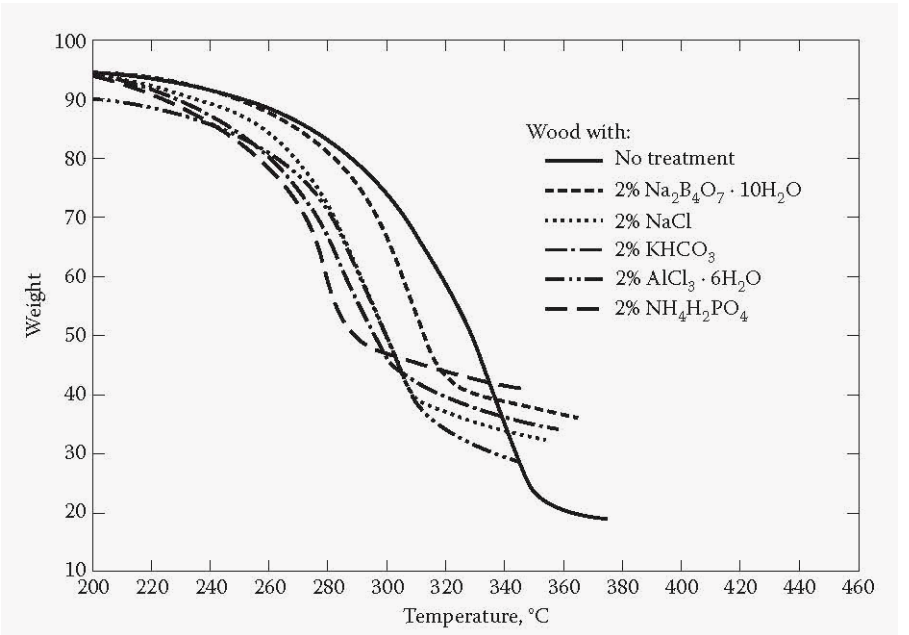

FIGURE 6.12 Thermogravimetric analysis of wood treated with various inorganic additives. (Adapted from Tang, W.K. and Eickner, H.W. 1968. *Effect of Inorganic Salts on Pyrolysis of Wood, Cellulose, and Lignin Determined by Differential Thermal Analysis.* USDA Forest Service Research Paper FPL 82, January.)

Figure 6.12 shows a TGA of untreated wood along with wood that has been treated with several inorganic fire retardants (Tang and Eickner 1968). Fire retardant chemicals such as ammonium dihydrogen orthophosphate greatly increase rate of hydrolysis of glycosidic bonds, increase the amount of residual char and lower the initial temperature of thermal decomposition. The amount of noncondensable gasses increases at the expense of the flammable tar fraction. The chemical mechanism for the reduction of the combustible volatiles involves 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 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 and ammonium dihydrogen orthophosphate increased both the char yield and the aromatic carbon content of the char (Table 6.9).

Figure 6.13 shows the TGA of untreated cellulose along with cellulose that has been treated with several inorganic fire retardants (Tang and Eickner 1968). The thermal decomposition pattern for

TABLE 6.9
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

Source: Adapted from Shafizadeh, F. 1984. *Advances in Chemistry Series*, Number 207, American Chemical Society, Washington, DC. Chapter 13: pp. 489–529; Nanassy, A.J. 1978. *Journal Wood Sci.* 11(2): 111–117.

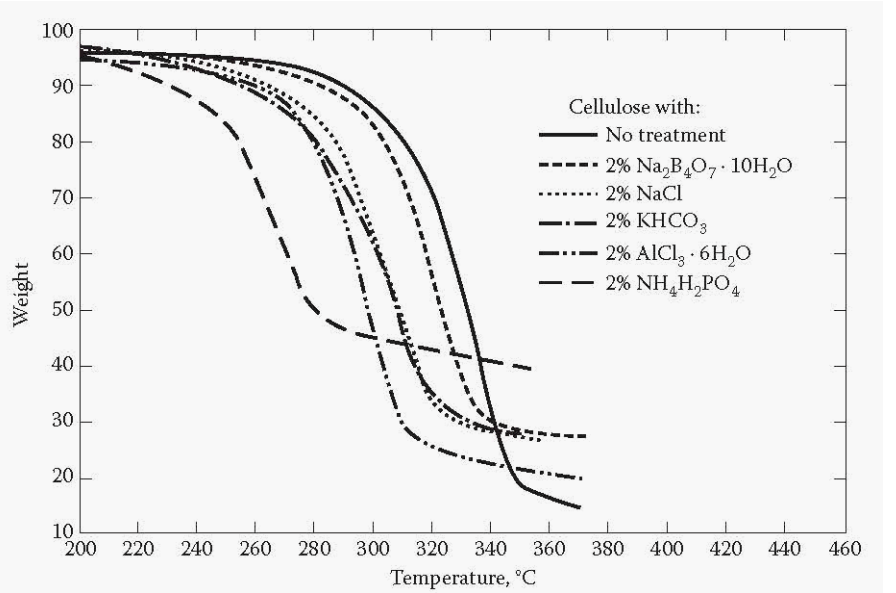

FIGURE 6.13 Thermogravimetric analysis of cellulose treated with various inorganic additives. (Adapted from Tang, W.K. and Eickner, H.W. 1968. *Effect of Inorganic Salts on Pyrolysis of Wood, Cellulose, and Lignin Determined by Differential Thermal Analysis.* USDA Forest Service Research Paper FPL 82, January.)

cellulose is similar to whole wood except 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 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 2 min of heating at 150°C with wood treated with ammonium dihydrogen orthophosphate. The DP dropped from 1300 to 700 after 1 h of heating borax treated wood at 150°C. Both of these chemical treatments suppressed the formation of levoglucosan (see Table 6.8).

Figure 6.14 shows the TGA of untreated lignin along with lignin that has been treated with several inorganic fire retardants (Tang and Eickner 1968). 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 > C1 > F. A mechanism for the inhibition of the chain-branching reactions using HBr as the halogen is:

$$H^{\cdot} + HBr \rightarrow H_2 + Br^{\cdot}$$
$$OH^{\cdot} + HBr \rightarrow H_2O + Br^{\cdot}$$

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

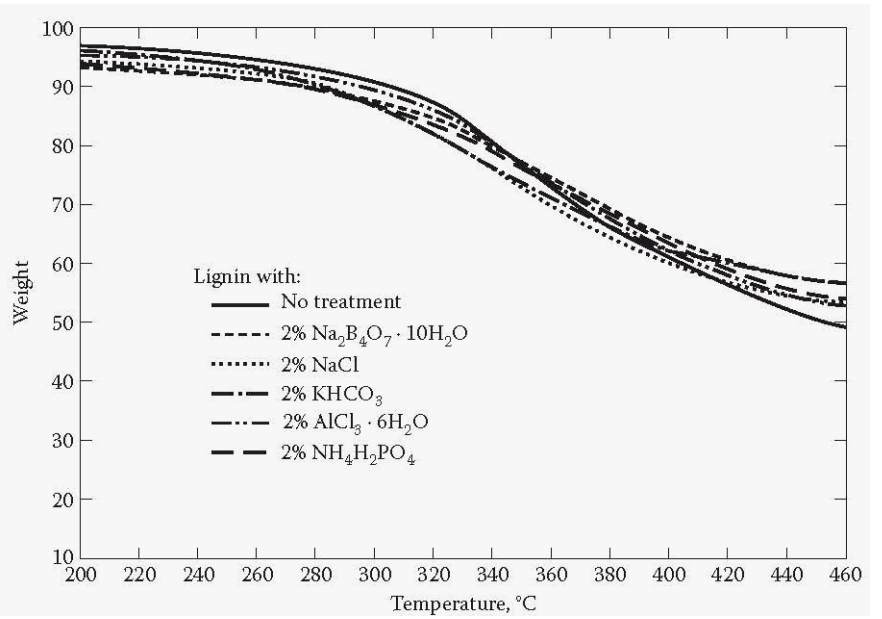

FIGURE 6.14 Thermogravimetric analysis of lignin treated with various inorganic additives. (Adapted from Tang, W.K. and Eickner, H.W. 1968. *Effect of Inorganic Salts on Pyrolysis of Wood, Cellulose, and Lignin Determined by Differential Thermal Analysis.* USDA Forest Service Research Paper FPL 82, January.)

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

$$O^{\cdot} + Br_2 \rightarrow BrO^{\cdot} + Br^{\cdot}$$
$$O^{\cdot} + OBr^{\cdot} \rightarrow Br^{\cdot} + O_2$$

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:

$$BrO^{\cdot} + {}^{\cdot}OH \rightarrow HBr + O_2$$
$$BrO^{\cdot} + {}^{\cdot}OH \rightarrow Br^{\cdot} + HO_2$$

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 combustion and flaming combustion by preventing the flammable products from escaping and by 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 carbonaceous foam and consist of several components. These compounds include 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, 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, guanidine, and 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 nontreated wood until the melt temperature is reached (Browne 1963). Above the melt temperature of the metal alloy, the rise in temperature is the same for treated and nontreated wood. Or one could use wood adhesives to fill in the voids of the wood to increase the density for higher thermal conductivity as well as provide blockage to volatile emissions from the subsurface pyrolysis zones.

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 the water is vaporized. This serves to remove heat from the pyrolysis zone thereby slowing down the pyrolysis reactions. 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 Noncombustible Gases

Chemicals such as dicyandiamide and urea release large amounts of noncombustible gasses 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 gasses would be beneficial because it increases the volume of combustible volatiles needed for ignition. Also the movement of gasses away from the wood may dilute the amount of oxygen near the boundary layer between the wood and the vapor-phase reaction that leads to flame extinction. The large emission of water vapor from the dehydration of gypsum boards at temperatures below the wood's degradation temperatures can be a big help for the veneer-like panels installed over the gypsum board, or even with a wood/gypsum composite.

6.4.6 Chemicals that Reduce the Heat Content of the Volatile Gases

As seen in Section 6.4.1 before, the addition of inorganic additives lower the temperature at which active pyrolysis begins and this resulting decomposition leads to increased amounts of char and reduced amounts of volatiles. This increased amount of char and reduced volatiles is due to the increased dehydration reactions, mainly the cellulose component of wood. However, other competing reactions also occur such as decarbonylation, decomposition of simpler compounds, and condensation reactions. All 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. Or one could test these treated materials in the cone calorimeter that provide information on the reduction of heat content as well as provide other properties needed to relate to flammability on a large scale (Schartel and Hull 2007, Dietenberger and White 2001).

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°C and 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 are attributed to the flaming of volatile products; the second exotherm, at 440°C for wood and 445°C for cellulose and 445°C for lignin are attributed to glowing combustion of the residual char (Tang 1964).

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, increase the glowing exotherm and shows a second glowing peak around 510°C. Sodium chloride also reduces the first exotherm, 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 reducing the amount of volatile products and also reduces the temperature where these products are formed. Ammonium phosphate almost eliminates the glowing exotherm (Tang and Eickner 1968).

Fire retardants 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 as a 29% release of accumulated 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 (Tang and Eickner 1968).

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. Many fire retardant formulations are water leachable and corrosive so research continues to find more leach resistant and less corrosive formulations.

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

TABLE 6.10
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

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 (1) guanyl urea phosphate (GUP) and boric acid (BA), and (2) phosphoric acid, boric acid, and ammonia. Table 6.10 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 pints 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 6.10 shows that wood treated with boric acid shows a weight loss of 81% and borax 89% weight loss at 500°C which is not as effective as phosphorus compounds. Indeed, the combination of GUP and BA was particularly studied because they are considered environmentally acceptable, relatively low in toxicity, relatively noncorrosive, relatively nonhygroscopic, and can be stored relatively long times (Gao et al. 2006). They found a strong synergistic effect between GUP and BA to significantly reduce both HRR and THR of treated wood tested in the cone calorimeter.

6.4.9 Leach Resistant Fire-Retardants

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 (i.e., 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 can 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 or melamine, 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, 5.10). In another approach, urea and DAP was delivered to the fibers via sol-gel technology that was synergistic in effectively reducing cotton clothing flammability and reducing leaching losses of the FRTs (Chapple and Barkhuysen 2005).

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