THEORIES OF THE COMBUSTION OF WOOD AND ITS CONTROL

A Survey of the Literature

By

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Introduction

As a rule wood does not burn directly (44, 79, 114).[2] It first undergoes thermal degradation, or pyrolysis -- some of the products of which are combustible gases, vapors, or mists. Under appropriate conditions the products may be set afire and, if enough of their heat of combustion is retained by the wood to maintain the pyrolysis, the burning may continue of its own accord until the wood has been consumed except for inorganic products left as ash. Ordinarily wood is set afire by bringing to bear enough heat to start active pyrolysis, and then applying a pilot flame or other source of high temperature to the combustible gaseous products after they have escaped and become mixed with air. In the absence of a pilot flame, much more heat must be supplied before the pyrolysis products will take fire spontaneously. The minimum rate of heating necessary for ignition by pilot flame is of the order of 0.3 calorie per square centimeter per second, but for spontaneous ignition it is of the order of 0.6 calorie per square centimeter per second (68).

Wood may be said to burn directly if its surface is irradiated so intensely that the temperature is raised to the point of spontaneous ignition within a fraction of a second, so that pyrolysis and combustion are practically simultaneous. Even then direct combustion is confined to a thin surface layer. Thin sheets of alpha cellulose that are exposed to short pulses of radiant power of 20 to 30 calories per square centimeter per second lose only part of their thickness in flame, leaving an extremely shallow layer of char that is backed by apparently unchanged cellulose (79). Direct combustion of explosive violence can occur

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[1] Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

[2] Underlined numbers in parentheses refer to Literature Cited at the end of this report.

when fine, dry particles of wood are distributed in air in such proportions that each particle is in contact with enough oxygen for its combustion and is close enough to its neighbors to ignite them quickly, in a manner analogous to a branching chain reaction (<u>44</u>).

<u>The Course of Pyrolysis</u>

The present interest is in normal combustion preceded by pyrolysis, When a piece of wood is heated out of contact with air, zones (<u>44</u>, <u>79</u>, <u>84</u>) develop parallel to the heat-absorbing surface, delimited by temperatures attained. The zones are well marked in wood because of its relatively low thermal conductivity <u>(75)</u> and density and relatively high specific heat (<u>22</u>).

<u>Zone A, up to 200° C.</u>

A layer of wood at the surface becomes dehydrated and evolves water vapor with perhaps traces of carbon dioxide, formic and acetic acids (<u>58</u>, <u>65</u>, <u>98</u>), and glyoxal (<u>33,116</u>).

<u>Zone B, 200° to 280° C.</u>

Zone A moves farther into the piece of wood and is succeeded by zone B in which pyrolysis remains slow (<u>35</u>, <u>43</u>, <u>138</u>). Water vapor, carbon dioxide, formic and acetic acids, glyoxal, and perhaps a little carbon monoxide are evolved (<u>79</u>, <u>83</u>, <u>95</u>) and additional vapors from zone A pass through. Thus far the reactions are endothermic (<u>58</u>, <u>138</u>) and the gaseous products are largely noncombustible. The wood slowly becomes charred (<u>76</u>, <u>81</u>).

<u>Zone C, 280° to 500° C.</u>

Zones A and B move inward to be succeeded by zone C in which active pyrolysis begins suddenly and exothermically (<u>43</u>, <u>44</u>, <u>58</u>, <u>98</u>, <u>118</u>). The temperature mounts rapidly unless the heat envolved is dissipated. Combustible gases and vapors -- notably carbon monoxide, methane, formaldehyde, formic and acetic acids, methanol, and later hydrogen -- diluted with carbon dioxide and water vapor (<u>9</u>, <u>17</u>, <u>59</u>, <u>70</u>, <u>79</u>, <u>95</u>) are enclosed forciblv enough to carry with them droplets of highly inflammable tars (<u>44</u>) that appear as smoke (<u>24</u>). The residue left in zone C becomes charcoal. The primary pyrolysis products undergo further pyrolysis and reactions with one another before they escape (<u>59</u>,

<u>6 5</u>, <u>7 9</u>, <u>1 1 8</u>). Such secondary reactions may be catalyzed by the charcoal, which is epecially active when formed at these temperatures (<u>5</u>). The second-ary pyrolysis of the tars is especially strongly exothermic (<u>5 9</u>). In commer-cial wood distillation, the temperature is kept within zone C until zones A and B vanish after reaching the center of the piece (<u>3 5</u>), and until the tars are ex-pelled. At this stage the process again becomes endothermic (<u>5 8</u>, <u>1 1 8</u>). Smok-ing ceases before 400° C. is reached at the center of the Piece (<u>2 4</u>). Carboni-zation is considered complete at 400° (<u>5 8</u>) to 600° C. (<u>3 5</u>, <u>8 7</u>). The fibrous structure of wood is retained despite serious changes in composition up to 300° C. (<u>1 3</u>, <u>3 5</u>, <u>1 3 0</u>). Above 400° C. the crystalline structure of graphite is developed (<u>9</u>, <u>1 9</u>, <u>3 9</u>).

<u>Zone D, Above 500° C.</u>

If the surface temperature continues to rise before carbonization becomes complete, zone D -- composed of charcoal -- becomes the seat of still more vigorous secondary reactions in which the gaseous products and tars rising from the zones underneath are further pyrolyzed to more highly combustible products. For example, carbon dioxide and water vapor react with carbon to form carbon monoxide, hydrogen, and formaldehyde (<u>7 9</u>).

<u>The Course of Combustion</u>

The course of events when wood is heated in air is similarly zonalized but is modified by oxidation reactions and, after ignition, by combustion of pyrolysis and oxidation products.

<u>Zone A, up to 200° C</u>.

The gases evolved by very slow pyrolysis are not ignitible. The wood loses weight steadily if only slowly (<u>7 6</u>, <u>1 2 0</u>). Above temperatures as low as 95° C. the wood eventually becomes charred (<u>7 6</u>, <u>8 1</u>). Oxidation reactions occur that are exothermic and may lead, under conditons in which the heat is conserved, to self-heating and even to self-ignition (<u>6</u>, <u>8 1</u>). Sound wood, however, does not ignite within zone A.

<u>Zone B, 200° to 280° C.</u>

Although the gases evolved still are not readily ignitible, an exothermic condi-tion is reached at lower temperatures than in pyrolysis out of contact with air.

The temperature at which the overall reactions of pyrolysis and oxidation become detectably exothermic has been taken as one of several definitions of the ignition point of wood (11, 131), even though spontaneous flaming does not begin until higher temperatures are reached (24). The exothermic point has been reported variously as 235° to 240° C. (131), 232° to 260° C. (37), 192° to 220° C. (11), and even as low as 150° C. (24). The variations indeterminations come lagely from the fact that time as well as temperature is involved in ignition at such low temperatures (26, 46, 81,131).

Prince (103) and McNaughton (81) reported that the gases evolved from wood can be ignited by a pilot flame 180° C. after heating for 14 minutes or at 250° C. after heating for 4 to 9.5 minutes, but their measurements may be seriously in error. These temperatures were measured in an air space, freely ventilated by convection, between the wood surface and a hot plate, the temperature of which was not recorded but must have been significantly higher. Absorption of radiant energy and heat evolved by oxidation in the exposed wood undoubtedly raised its temperature well above that of the moving air current. The wood charred before it inflamed and the charcoal layer was highly absorptive of heat and exothermically reactive with oxygen (5, 90). The actual temperature of the wood surface when flaming began was probably well beyond the limits of zone B.

Fons (26), by measuring the temperature at two different depths beneath the surface of ponderosa pine and applying the equation for thermal conduction, found that the temperature of the wood at the exposed surface was 343° C. when it burst into flame. In air between 232° and 443° C. the wood was reduced to charcoal without flame, after which the charcoal began to glow, still without flame.

Zone C. 280° to 500° C.

The mixture of gases copiously evolved in zone C at first should be too rich in carbon dioxide and water vapor to sustain flame, but it soon becomes more combustible as a result of secondary pyrolysis (79). The gases may then be readily ignited by a pilot flame and burn steadily in luminous diffusion flames. At this stage flaming combustion occurs entirely in the gas phase outside the wood because the rapidly emerging gases lack necessary oxygen until they have gone far enough to mix with air in proportions between the lower and upper limits of flammability (77). Indeed, under suitable conditions the flaming combustion may occur at a considerable distance from the wood.

Self-sustaining diffusion flames from organic fuels burn at 1100° C. or somewhat more (30). One-half to two-thirds of the heat of combustion of wood is

liberated in flaming, the balance in glowing combustion of the charcoal (14). How much the heat of flaming contributes to the spread of combustion depends on such external conditions as the geometry of the situation and the velocity of the air. A vertical stick less than 3/4 inch thick that is ignited at the lower end in still air may burn to the top but, in a strong wind or if ignited at the upper end, most of the heat is dissipated and the fire may go out. If the stick is more than 3/4 inch thick, it probably will not burn to the top even if ignited at the bottom in still air, unless external heat is applied (14). A single log in a fireplace will not keep burning without continuous supply of heat from flaming kindling or hot coals beneath it, but three logs properly spaced may keep burning as long as each contributes heat to the others.

As long as gases pour forth rapidly enough to blanket the wood surface to the exclusion of oxygen, the charcoal formed cannot burn and is left to accumulate. Since charcoal has only one-third to one-half of the thermal conductivity of wood, the layer of charcoal retards penetration of heat and delays attainment of the exothermal point in the wood underneath (84, 113). Thus, after the first vigorous flaming of wood, there is often a diminution of flaming until sufficient heat has passed through the insulating layer of charcoal to pyrolyze deeper portions of the wood.

If there is no pilot flame or its equivalent to ignite the gases, there may be no flaming until pyrolysis in zone C is nearly complete and the emission of gases slows sufficiently to let air make contact with the charcoal layer. Since charcoal does not melt below 3480° C. or boil below 4200° C. (67), it cannot go forth to meet the air for its combustion, but must burn in place as air reaches it. Nevertheless, charcoal is an excellent absorber of radiant heat and has a lower temperature of spontaneous ignition than any of the other major products of pyrolysis. Thus temperatures of spontaneous ignition for mixtures with air between the limits of flammability are reported as 644° to 658° C. for carbon monoxide, 580° to 590° C. for hydrogen, 566° C. for acetic acid, 539° to 750° C. for methane, and 430° C. for formaldehyde (67). Pine tar is said to ignite spontaneously at 355° C. But for charcoal spontaneous ignition is reported at temperatures as low as 150° to 250° C. (5, 26, 90, 102). Even at 100° C. the combination of charcoal with oxygen generates 2.7 calories per cubic centimeter of oxygen reacting (5). The hot charcoal from the industrial distillation of wood in retorts takes fire if it is allowed to come in contact with air before it cools (43). When wood ignites spontaneously, it is therefore the charcoal that takes fire first (44, 26) late in zone C after the first vigor of emission of gases is over and air can reach the solid surface. The best measurements of surface temperatures for spontaneous ignition of wood agree with this view -- Lawson and Simms, 350° to 450° C. (68); Fire Research Board, 380° C. (24); Fons, 343° C. (26); Hawley, above 300° C. (44); Jones and Scott, 270° to 290° C. (52).

Zone D, Above 500° C.

At 500° C. (incipient red heat) the charcoal glows and is comsumed. The interior of the piece of wood may still be in zones B or C at much lower temperatures (3). When the surface rises somewhat beyond 1000° C. (yellowish-red heat), carbon is consumed at the surface as fast as the reaction zones penetrate into the piece (79). The luminous diffusion flames give way, as the reactions of primary wood pyrolysis become exhausted, to the nonluminous diffusion flames of burning carbon monoxide and hydrogen. When the supply of carbon monoxide and hydrogen finally fail, the remaining charcoal merely glows with little or no flame.
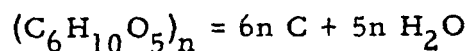
Pyrolysis Reactions

The relative proportions of gases, vapors, tars, and charcoal and the relative proportions of flammable and nonflammable gases produced will vary widely according to the conditions of temperature, pressure, time, geometry, and environment under which pyrolysis occurs. The yields of products may also be altered greatly by the presence of retardants or combustion catalysts in the wood or on its surface.

In carbonizing birch from an initial temperature of 250° C. to a final temperature of 400° C. at different rates and pressures, Klason (59) found the variations in yields of charcoal, tars, water, carbon dioxide, and carbon monoxide reported in table 1. Here pyrolysis at a pressure of 5 millimeters of mercury revealed very nearly the primary pyrolysis products because they were removed from the reaction zone before there had been much time for secondary pyrolysis. Less than 20 percent of the wood was left as charcoal and nearly 40 percent was converted to tars, which are highly combustible. At atmospheric pressure the yield of charcoal rose and that of tars declined, the more so the slower the pyrolysis. For very slow pyrolysis the yield of charcoal doubled, whereas that of tars nearly vanished. Secondary pyrolysis therefore converted tars into gases and tar coke, the latter being weighed as part of the charcoal. Careful computation of the thermal balance (56, 59) revealed that the primary pyrolysis in vacuo is not exothermic but consumes heat. The liberation of heat under ordinary conditions comes from strongly exothermic pyrolysis of the tars. The secondary reactions increase the quantities of water and carbon dioxide in the gaseous products without increasing the quantity of carbon monoxide. Thus rapid pyrolysis, such as necessarily occurs when wood burns, produces more flammable tars and gases, less diluted with water and carbon dioxide, than does slow pyrolysis.

Industrial distillation of wood in retorts in the course of 16 to 24 hours commonly yields 40 to 50 percent of charcoal (1, 43, 57). Carbonization of sawdust in 25 minutes in a rotary kiln produces 23 to 26 percent charcoal (106, 108). Carbonization of sawdust in 7 to 8 minutes in a multiple-hearth furnace gave 21 percent charcoal (34). In laboratory tests, small birch blocks, which were carbonized in less than 1 minute in an atmosphere of nitrogen to preclude loss by oxidation, yielded only 12.75 percent charcoal of composition similar to that of industrial charcoal (34). Moreover, chemicals impregnated into wood may alter the yields of tars and charcoal, as is described farther on.

Rapid heating through the range of active pyrolysis tends to produce little charcoal, much tar, and highly flammable gases that are rich in hydrogen, carbon monoxide, and hydrocarbons; slow heating tends to produce much charcoal, little tar, and less flammable gases in which there is much water and carbon dioxide (79). In slow heating, decomposition proceeds in an orderly manner in which there is stepwise formation of increasingly stable molecules, richer in carbon and converging toward the hexagonal structure of graphitic carbon (9, 39, 87). In very rapid heating, macromolecules may be literally torn into volatile fragments with little possibility of orderly arrangement (79).

The chemical theory of flameproofing wood and other cellulosic materials (15, 20, 23, 36, 48, 69, 114, 115) is based on changing the pyrolysis mechanism from that of pyrolysis to that of slow pyrolysis. If the pyrolysis of the cellulose could be directed to complete dehydration (69) according to the equation:

$$(C_6H_{10}O_5)_n = 6n\ C + 5n\ H_2O$$

there would be no flammable gases from the major component of wood until temperatures were high enough for the water-gas reaction to set in, by which time most of the water would escape.

The slow and fast reactions of pyrolysis for cellulose, together with the heats of formation (ΔH_f) involved, have been represented schematically (79) as follows:

Volatile products	Heat of formation ΔH_f (cal. per mg.)
H_2O	- 3.21
CO_2	- 2.14
RCOOH	- 1.9
CO	- 0.93
RCHO	- 0.9
CH_2CO	- 0.36
ROH	- 1.3
CH_4	- 1.0
C_2H_6	- 0.66
H_2	0
C_2H_4	+ 0.45
C_2H_2	+ 2.1
free radicals: CH, CH_2, CH_3, CHO, C_2	+ 2 to 10

Carbon $(\Delta H_f = 0)$ +

Cellulose $(\Delta H_f = -1$ to -1.5 cal. per mg.)

slow pyrolysis

fast pyrolysis

Thus slow pyrolysis yields charcoal and oxygenated gases and vapors of low flammability and releases energy, whereas fast pyrolysis yields little or no carbon, forms hydrogenated gases and vapors, and consumes energy.

The pyrolysis of wood (**39, 10, 120, 139**) and other cellulosic materials (**64, 78, 79, 91**) follows reasonably closely the kinetics of a first-order reaction. It is "diffusion-controlled" rather than rate-controlled," the rate being determined by the rate of energy transfer within the solid rather than by the rate of pyrolysis (**79**). There are satisfactory kinetic data for slow pyrolysis of wood below the exothermic region and for other cellulosic materials both below and above the exothermic region. Such data are given in table 2. Martin (**79**), on the basis of the data of Stamm (**120**) and of Kujirai and Akahira (**64**) in table 2, saw evidence of an expected alteration in kinetics on passing from slow pyrolysis below the exothermic region to fast pyrolysis above it. He suggested that the kinetics may be formulated as follows:

$$-\frac{dw}{dt} = \left(k_1 A_1 e^{-E_1/RT} + k_2 A_2 e^{-E_2/RT}\right) w$$

in which $\underline{w}$ is the weight of wood remaining after time, $\underline{t};\underline{k_1}, A_1,$ and E_1 are respectively the specific rate constant, frequency factor, and activation energy for the slow pyrolysis, and k_2, A_2, and E_2 are the corresponding parameters for the fast pyrolysis; $\underline{R}$ is the gas constant, $\underline{T}$ the absolute temperature, and $\underline{e}$ the base of Napierian logarithms. Constant $\overline{k_2}$ would begin to predominate at 400° C. if A_2 is about 10^{20} per second and $\overline{E_2}$ is about 50 kilocalories per mole. It is therefore interesting to find in table 2 that Madorsky, Hart, and Straus (78) in later work found activation energies of 45 to 50 kilocalories per mole for various cellulosic materials when pyrolyzed at higher temperatures. Discussion of the effect on activation energy of impregnation with added chemicals, as shown in table 2, belongs to the section of this report on possible mechanisms of chemical action of retardants.
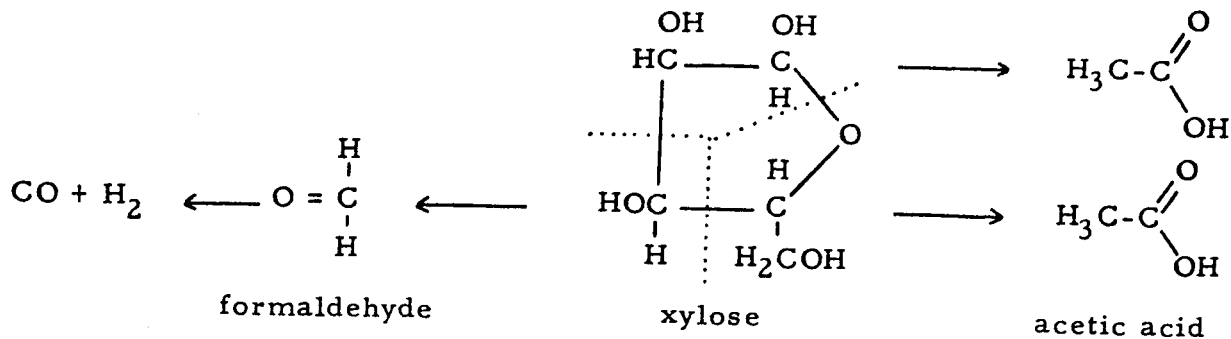

Pyrolysis of Wood Components

The yield of products when wood has been completely pyrolyzed is about what would be obtained by pyrolyzing separately the proportional amounts of the major wood constituents -- hemicellulose, cellulose, and lignin (23, 35, 70). Breakdown of the components, however, is not entirely simultaneous. The hemicellulose, particularly its pentosans, are said to decompose first) largely between 200° and 260° C., followed by the cellulose at 240° to 350° C., and finally by the lignin at 280° to 500° C. (43, 63, 65, 83, 89). Some investigators accordingly report three peaks in the exothermic region (63, 93, 95, 118, 124).
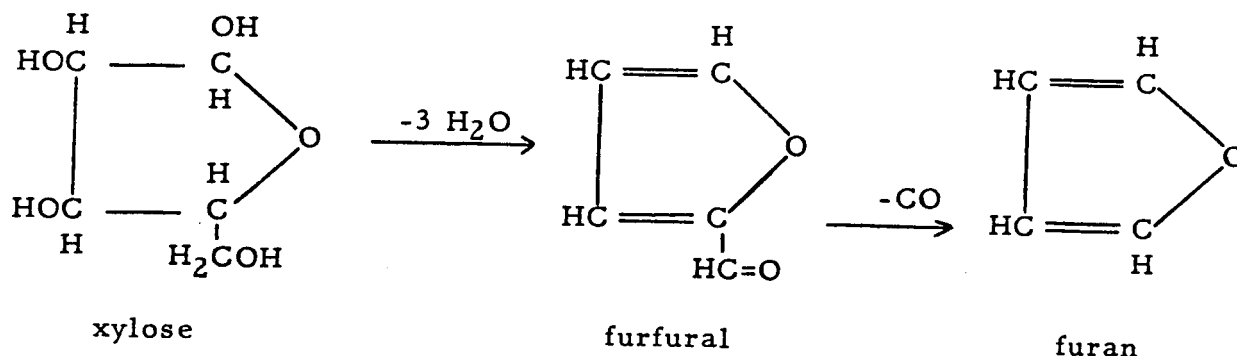

Hemicellulose

Hemicellulose evolves more gases, less tar, and about as much aqueous distillate as are formed from cellulose, but differs from cellulose in that hemicellulose yields no levoglucosan (50, 92).

Much of the acetic acid formed in pyrolysis of wood is attributed to the hemicellulose (54, 61, 88). Scission of a carbon-to-oxygen bond in a pentose might lead to further splitting to acetic acid and perhaps formaldehyde or carbon monoxide and hydrogen:

$$CO + H_2 \xleftarrow{\quad} O = \underset{H}{\overset{H}{\underset{|}{C}}} \xleftarrow{\quad} \text{xylose} \xrightarrow{\quad} H_3C-C\overset{\displaystyle O}{\underset{\displaystyle OH}{<}} \quad H_3C-C\overset{\displaystyle O}{\underset{\displaystyle OH}{<}}$$

formaldehyde   xylose   acetic acid

Similar splitting of a hexose could produce three molecules of acetic acid.

Pentoses are also known to yield furfural and other furan derivatives (35, 83, 121). This production can occur readily by dehydration, to which carbohydrates are highly susceptible:

$$\text{xylose} \xrightarrow{-3\ H_2O} \text{furfural} \xrightarrow{-CO} \text{furan}$$
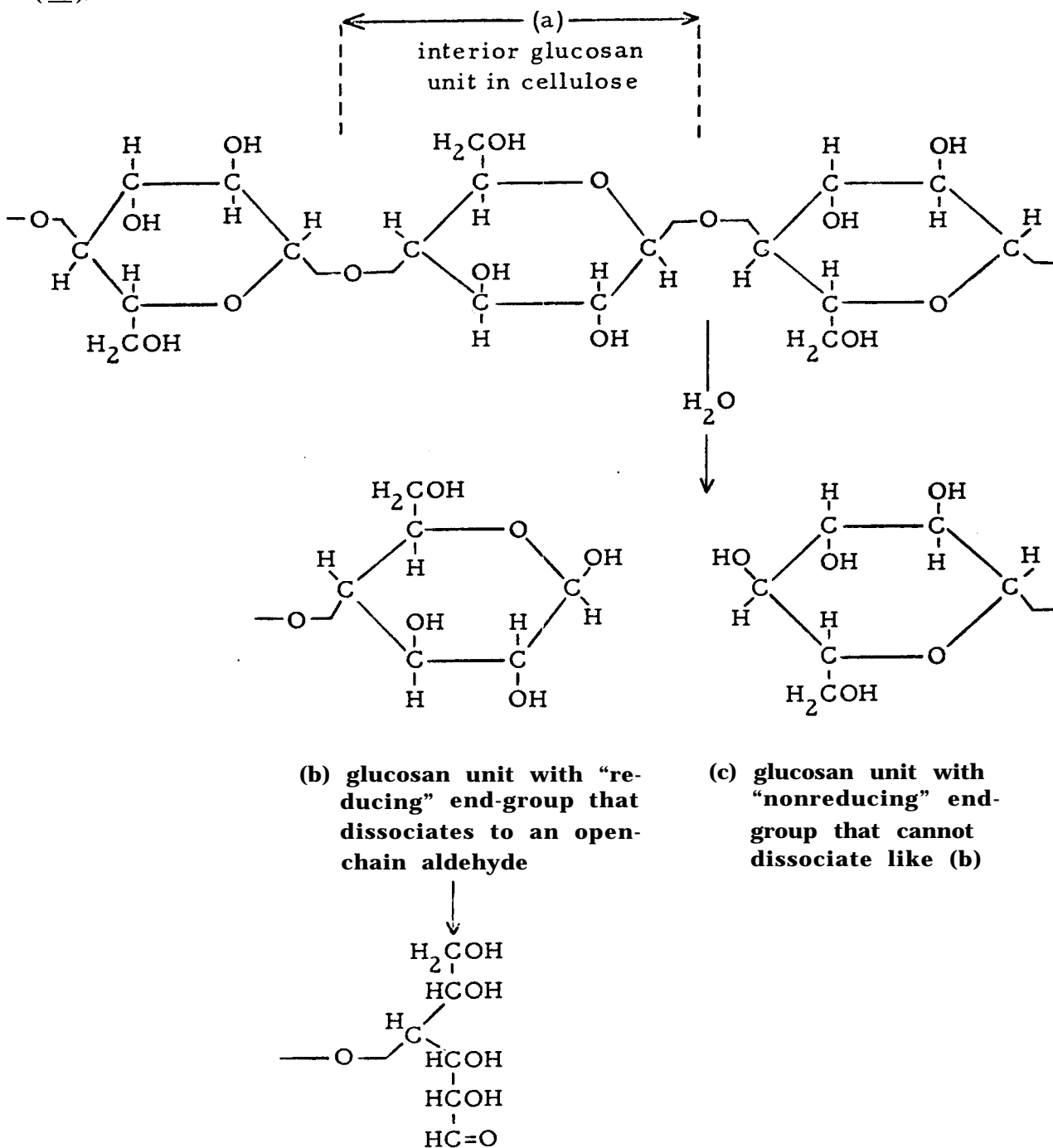
xylose   furfural   furan

Cellulose

Cellulose evolves water in the first stage of thermal decomposition before any other significant changes are observable. On the other hand, cellulose triacetate evolves acetic acid instead of water and fails to yield water even when pyrolysis is completed (78). Therefore, dehydration occurs with cellulose and deacetylation occurs with cellulose triacetate, presumably at random, along the chains of glucosan units.

Early in the pyrolysis of cellulose some of the carbon-to-oxygen bonds in the links between glucosan units may be expected to break at random points along the chain. Even at room temperature, cellulose is easliy hydrolyzed at these points, especially so in the presence of acids. In pyrolysis, water and acids are present from prior pyrolysis of the hemicellulose and from dehydration of the cellulose. Besides hydrolysis, pyrolytic scission may serve to break the links. The points in the cellulose macromolecules at which the first random breaks in the carbon-to-oxygen bonds take place and the way in which the

the fracture is brought about may govern very largely the subsequent course of pyrolysis of the fragments so produced.

Hydrolysis at one carbon-to-oxygen link in a cellulose macromolecule produces two shorter macromolecules, the new end groups of which differ in properties. One is a "reducing" end group that can dissociate to an open-form polyhydroxy aldehyde, whereas the other is a "nonreducing" secondary alcoholic end group (79):

(a) interior glucosan unit in cellulose

(b) glucosan unit with "reducing" end-group that dissociates to an open-chain aldehyde

(c) glucosan unit with "nonreducing" end-group that cannot dissociate like (b)

The interior glucosan units (a), the units with "reducing" end group (b), and the units with "nonreducing" end group (c), may be expected to behave differently on pyrolysis. Still further differences in behavior would be expected if the glucosan units had lost one or more molecules of water by dehydration before the hydrolytic cleavage of the carbon-to-oxygen links took place.

If both carbon-to-oxygen links of an interior glucosan unit (or the one link of a unit on the end of the chain) is hydrolyzed, a molecule of glucose is produced. Glucose can dehydrate to α -glucosan (1, 2 anhydroglucosan), which above 110° C. rearranges to β -glucosan or levoglucosan (1, 6 anhydroglucosan)   (<u>51</u>, <u>80</u>, <u>100</u>).

glucose

α-glucosan
(1, 2 anhydroglucose)
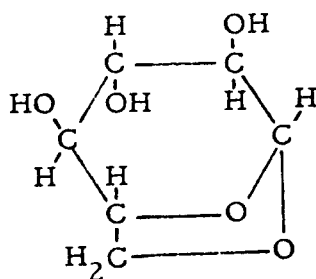
β-glucosan or
levoglucosan
(1, 6 anhydroglucose)
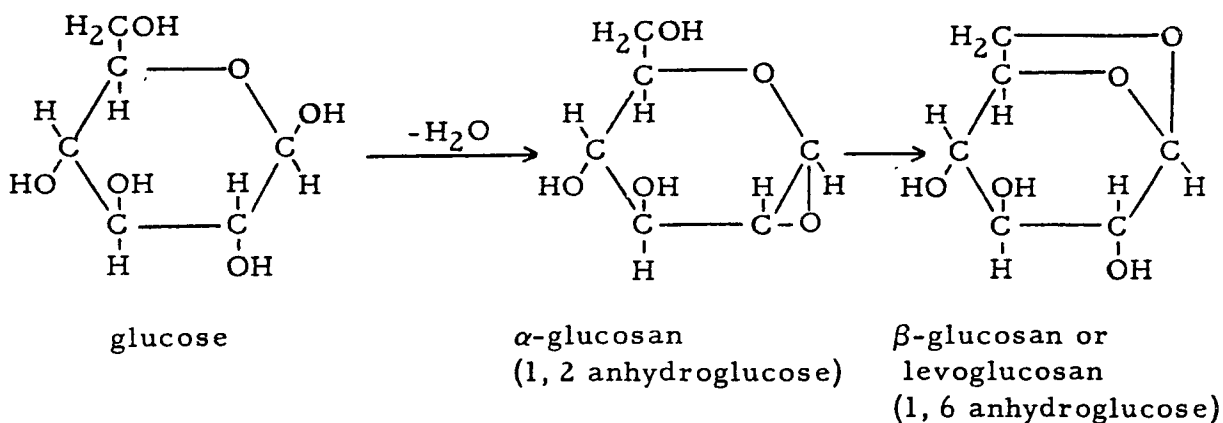
Levoglucosan is a characteristic product of the primary pyrolysis of cellulose and plays an important part in one of the modern theories of flameproofing cellulosic fabrics   (<u>115</u>).   Yields of levoglucosan as great as 50 to 53 percent, representing about one of every two glucosan units, have been obtained from pyrolysis of cellulose at 200° to 300° C. in vacuo   (<u>78</u>, <u>99</u>, <u>132</u>), and it has been found in lower yields at atmospheric pressure   (<u>78</u>, <u>116</u>, <u>126</u>). Presence of water-soluble inorganic impurities reduces or prevents formation of levoglucosan   (<u>132</u>) and it is not formed by pyrolysis of wood unless lignin is first removed, at least in part, by chlorination   (<u>92</u>). Levoglucosan melts at 180° C., remains stable up to 270° C., and then pyrolyzes to water, formic acid, acetic acid, and phenols   (<u>100</u>).

It is possible that the initial break in carbon-to-oxygen chain links may occur by random pyrolytic scission   (<u>78</u>) in stead of hydrolysis. If the breaks occur in bonds between oxygen and number 1 carbon atoms, levoglucosan may be formed by double Walden inversion   (<u>80</u>) with hydrogen atoms from alcohol groups of adjacent glucosan units wandering to the oxygen atoms thus servered:
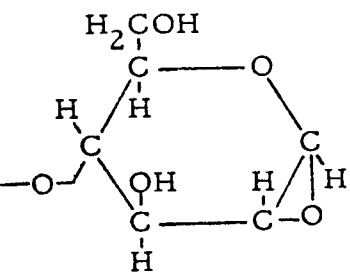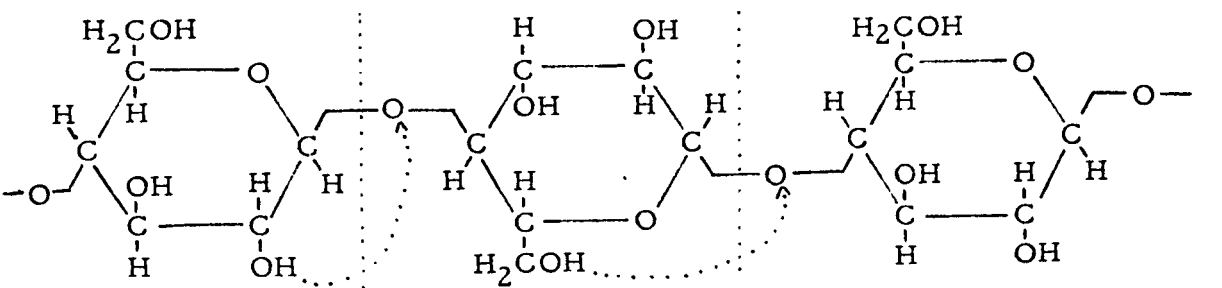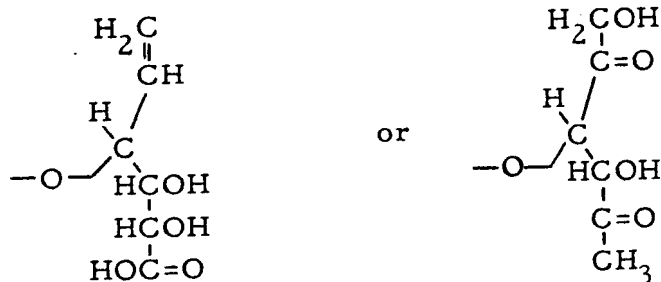
(d) anhydroglucose
unit

levoglucosan
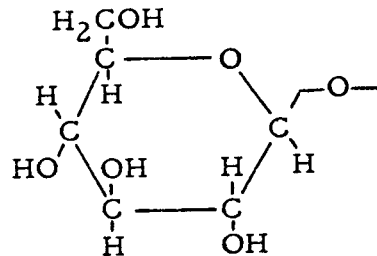
(c) glucosan unit with
"nonreducing" end
group

The anhydroglucose unit marked (d) resembles the (b) glucosan unit with "reducing" end group obtained in hydrolytic splitting of the chain. The (d) unit perhaps might open into polyhydroxy acids or polyhydroxy ketones of some such configurations as:
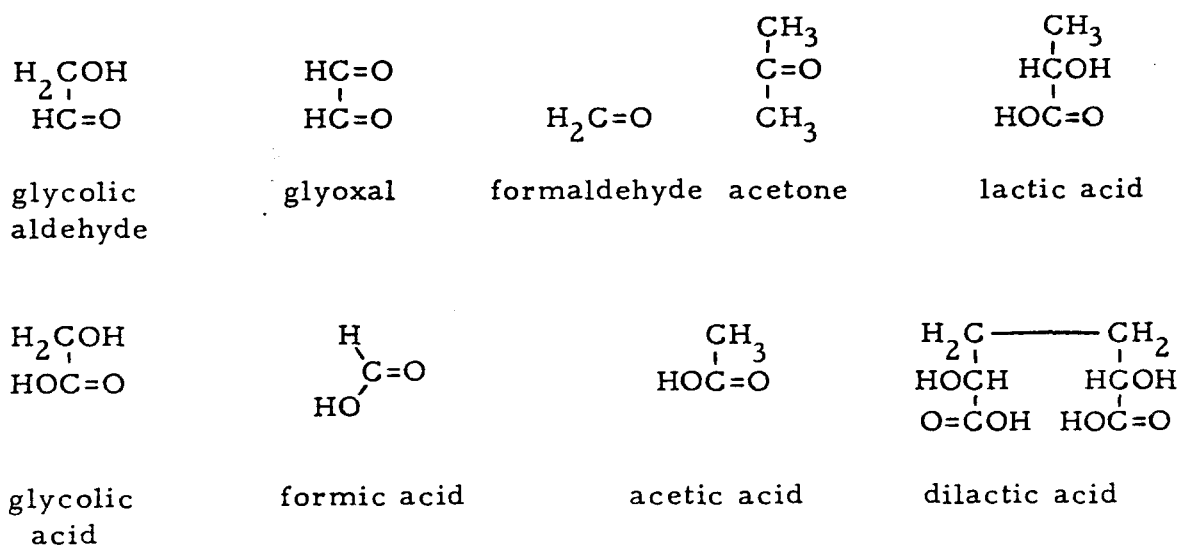
or

The glucosan unit marked (c) from pyrolytic scission is identical with the (c) unit from hydrolysis.

If pyrolytic scission breaks the bond between oxygen and number 4 carbon atom, instead of number 1, formation of levoglucosan is not possilbe. Madorsky, Hart, and Straus (78) consider that the maximum yield of approximate
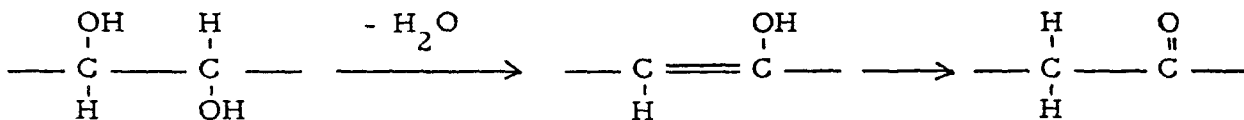
one molecule of levoglucosan for each two glucosan units indicates an even chance of pyrolytic scission on either side of the oxygen link. Scission between oxygen and carbon atom 4 presumably leaves the configuration so unstable that the glucosan ring decomposes to simple compounds such as water, carbon dioxide, and carbon monoxide, which always appear among the products. The same authors observe that neither the degree of crystallinity nor the degree of polymerization of the cellulose seem to affect pyrolysis appreciably because cotton cellulose, hydrocellulose made from it, viscose rayon, and cellulose regenerated from cellulose triacetate all pyrolyze at similar rates, with similar activation energies and similar yields of products.

After the initial breaking of cellulose macromolecules by hydrolysis or by pyrolytic scission, subsequent pyrolysis may proceed differently for the fragments that differ in their end groups. Open-chain polyhydroxy aldehydes, ketones, or acids formed by dissociation of fragments with "reducing" end groups, marked (b) or (d) in the preceding, might readily pyrolyze to simpler hydroxy aldehydes, ketones, or acids (79). Simultaneous oxidation-reduction of adjacent aldehyde and alcohol groups to form hydroxy acids or hydroxyketones is possible (50). In such ways it is possible to account for formation of formaldehyde, acetone, glyoxal, glycolic aldehyde, glycolic acid, lactic acid, dilactic acid, formic acid, and acetic acid, as well as water, carbon monoxide, and carbon dioxide, all of which have actually been obtained in substantial quantities from pyrolysis of cellulose (35, 116).

$$
\begin{array}{c}
H_2COH \\
HC{=}O
\end{array}
\qquad
\begin{array}{c}
HC{=}O \\
HC{=}O
\end{array}
\qquad
H_2C{=}O
\qquad
\begin{array}{c}
CH_3 \\
C{=}O \\
CH_3
\end{array}
\qquad
\begin{array}{c}
CH_3 \\
HCOH \\
HOC{=}O
\end{array}
$$

glycolic aldehyde   glyoxal   formaldehyde   acetone   lactic acid

$$
\begin{array}{c}
H_2COH \\
HOC{=}O
\end{array}
\qquad
\begin{array}{c}
H \\
C{=}O \\
HO
\end{array}
\qquad
\begin{array}{c}
CH_3 \\
HOC{=}O
\end{array}
\qquad
\begin{array}{c}
H_2C{-\!-\!-}CH_2 \\
HOCH \quad HCOH \\
O{=}COH \quad HOC{=}O
\end{array}
$$

glycolic acid   formic acid   acetic acid   dilactic acid

On further pyrolysis at higher temperatures, carboxyl groups yield carbon dioxide, a nonflammable flame-inhibitive gas, whereas aldehyde groups yield formaldehyde and then hydrogen and carbon monoxide, a highly flammable mixture.

The "nonreducing" end group marked (c) produced in hydrolysis or in pyrolytic scission differs from the interior groups marked (a) in having one extra unassociated alcoholic group (79). In the pyrolysis of units with either (a) or (c) groups, by analogy with other polyhydric alcohols, adjacent alcoholic groups might be expected to eliminate water:

$$
\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{-C}}\!\!-\!\!\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\;\;\xrightarrow{-\,H_2O}\;\;\underset{\underset{H}{|}}{\overset{\overset{OH}{|}}{-C}}\!\!=\!\!C-\;\longrightarrow\;\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{-C}}\!\!-\!\!\overset{\overset{O}{\|}}{C}-
$$

to form a ketone. In fact, dehydration of the cellulose in the very first stage of thermal decomposition may produce such ketones before hydrolysis or pyrolytic scission begins. Ketones commonly decompose thermally to ketenes (50), the simplest of which is formed by thermal decomposition of acetone:

$$
CH_3 \cdot CO \cdot CH_3 \longrightarrow CH_2 = C = O + CH_4.
$$
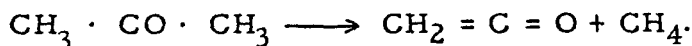
Ketenes have not been reported among the pyrolysis products of cellulose, but they are so reactive that no more than transient existence is to be expected. Nevertheless they may exert much effect on the course of pyrolysis. Since ketenes oxidize rapidly in air even at low temperatures, they may be expected to afford important sources of ignition.

More drastic dehydration of glucosan units may produce furan derivatives much as hydroxymethylfuraldehyde is known to result from loss of three molecules of water from glucose. Furaldehyde and furans have been identified among the pyrolytic products of wood (35, 83, 110, 121). Presence of catalysts that stimulate dehydration would be expected to favor such reactions.

Breaking of carbon-to-carbon bonds in glucosan units leaves unstable configurations that must rearrange or shed such fragments as CHOH or CHOH · CHOH, which must then take stable forms or break up further. CHOH · CHOH can form acetic acid (CH_3COOH), separate into ketene (CH_2CO) and water, or into methane and carbon dioxide.

At the temperatures of pyrolysis, the transitory existence of free radicals that can then participate in chain reactions is highly probable. Among such possible free radicals are CHO, CH_3, CH_2, H and OH. Because of their short lifetimes they could not be found as pyrolysis products, but they may well affect the course of pyrolysis reactions. In particular, the free radicals may exist long enough in the vapors from pyrolyzing wood to play a part in ignition in the region where the evolving vapors. mix with air.

Not all of the pyrolytic reactions in cellulose proceed in the direction of break-up into smaller molecules and molecular fragments. There is a conversion of part of the cellulose into a substance closely resembling lignin (33, 43, 83, 89, 110) and some aromatization and aromatic condensation of the decomposition products (39, 65). This may furnish the clue to formation of high-boiling components of the tars produced in pyrolysis. For example, phenolic compounds presumably would condense readily with aldehydes to form resinous substances.
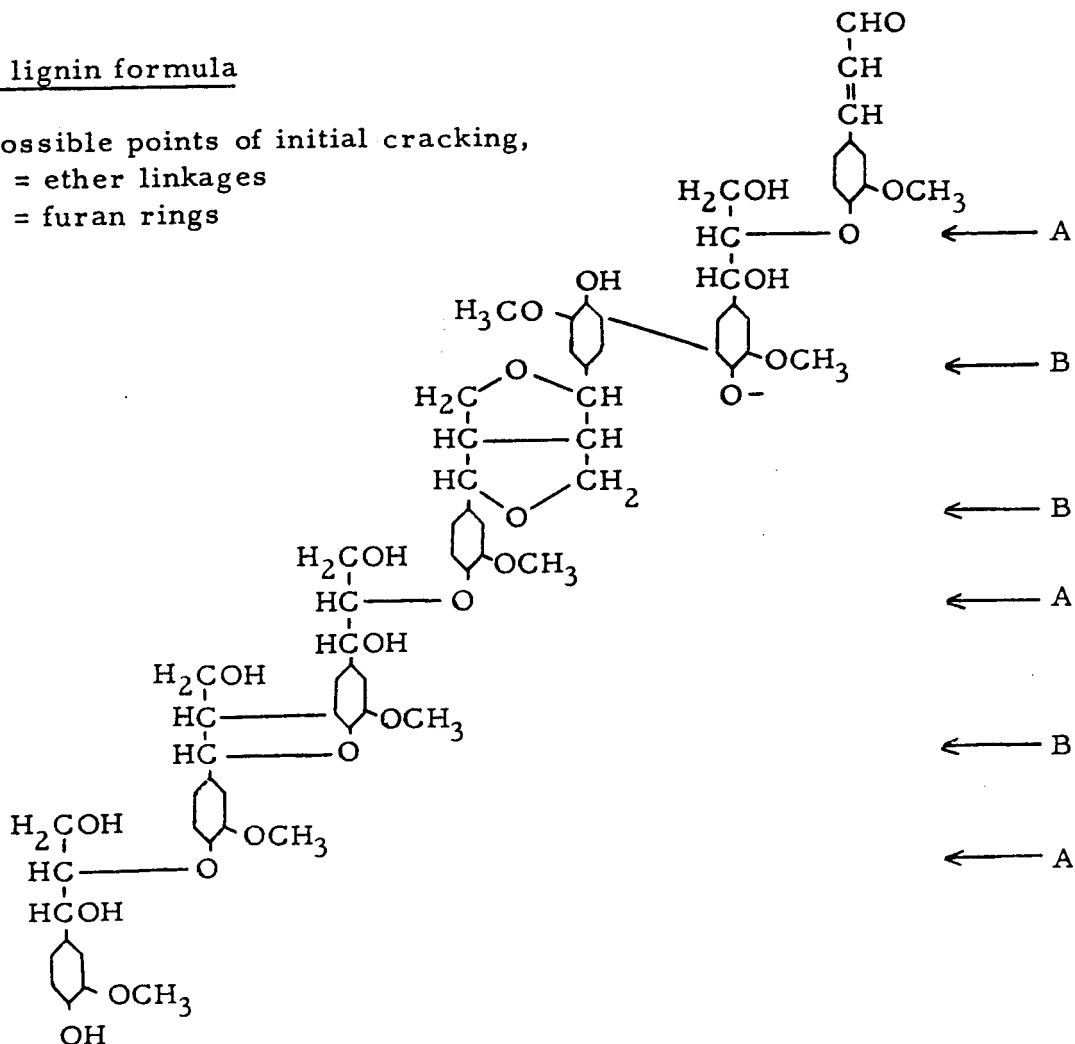
Lignin

Lignin on pyrolysis is particularly productive of aromatic products (25, 28, 54, 65 and yields more charcoal than is obtained from cellulose (8, 25, 35, 70). Lignin does not form a characteristic major product of its intial pyrolysis corresponding to the levoglucosan from cellulose. Such Difference might be expected since lignin presumably is built up of a variety of simpler units, whereas cellulose is more nearly a condensation polymer of repeated, identical units. Nevertheless, the primary products of pyrolysis of lignin are closely related structurally to the formulas attributed to lignin (28).
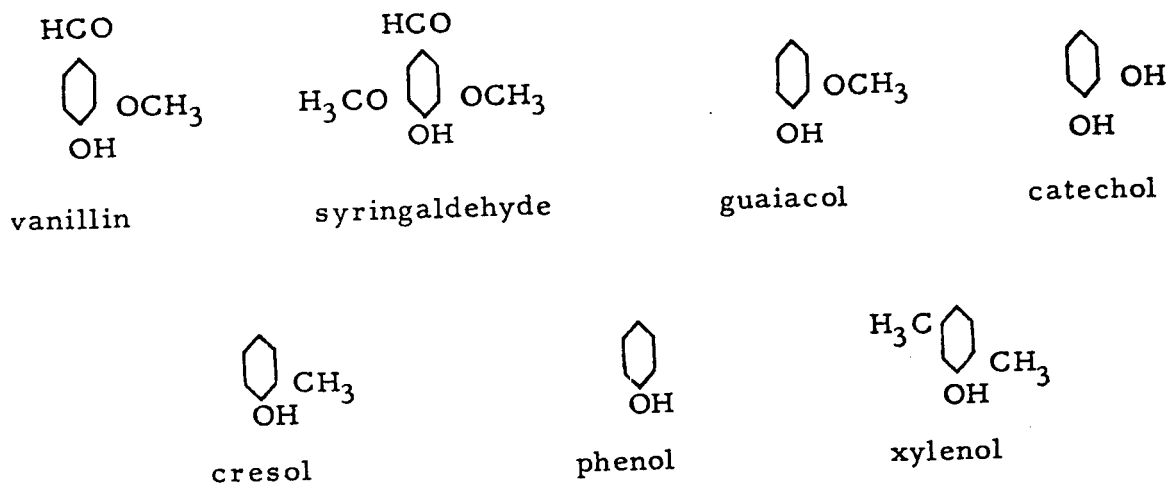
Adler's lignin formula

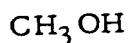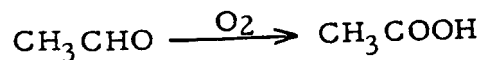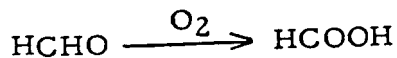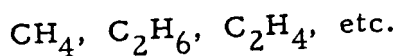Possible points of initial cracking,
A = ether linkages
B = furan rings

Products formed from aromatic nuclei:

vanillin

syringaldehyde

guaiacol

catechol

cresol

phenol

xylenol

Products formed from straight-chain fragments:

$$CO \xrightarrow{O_2} CO_2$$

$$CH_4, \ C_2H_6, \ C_2H_4, \ \text{etc.}$$

$$HCHO \xrightarrow{O_2} HCOOH$$

$$CH_3CHO \xrightarrow{O_2} CH_3COOH$$

$$CH_3OH$$
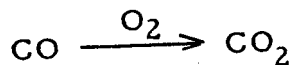
Apparently initial breakdown occurs chiefly in the straight-chain links connecting such aromatic units as the vanillyl, syringyl, and guaiacyl groups. The aromatic units give rise to phenols, xylenols, guaiacols, cresols, and catechols. the streaight-chain links produce carbon dioxide, hydrocarbons, formic acid, acetic acid, higher fatty acids, the methanol (8, 28, 3 5).

The pyrolytic products first formed from hemicellulose, cellulose, and lignin promptly undergo further reactions, not all of which are pyrolytic. Polymerizations and condensation reactions to form more complex molecules -- such as high-boiling tars, waxes and resinous substances with perhaps phenol-formaldehyde-type lingkages -- are also involved (25, 35, 39, 65, 118). Goos (35) lists 213 compounds that have been indentified in the liquid products of destructive distillation of wood.

The great complexity of the primary pyrolysis of wood and the succession of secondary reactions readily account for the wide variations in yields of gases, vapors, tars, and charcoal according to the particular conditions under which pyrolysis takes place. Such variability in results, however, offers hope that sufficient knowledge of the factors that control the course of the primary pyrolysis might lead to improved methods of making wood more resistant to fire. In this connection it is especially significant that small amounts of impurities or additives are already known to exert profound effects. The yield of levoglucosan in pyrolysis of cellulose is very sensitive to water-soluble inorganic impurities in the cellulose (78,132). As little as 1.3 percent of sulfuric acid in lignin increases the yield charcoal and decreases the yield of tars (25). Treatment of wood with phosphoric acid (41,96) or with magnesium chloride, zinc chloride, aluminum chloride, iron sufide, or cobalt sulfide (7) increases the yield of charcoal and decreases the yield of tars. The first four of these chemicals, at least, have been found to exert fire-retardant action (49,128,129). On the other hand, sodium carbonate (41), lime, alumina, thoria, zinc oxide, and chromium oxide either decrease the yield of charcoal (7) or have little effect on the yield (112), and have been found inferior in fire retardance (49) when used as impregnants. But in pyrolysis of cotton cellulose, impregnation with sodium carbonate or with sodium chloride was found to increase the yield of charcoal and decrease the yield of tar (78). Potassium carbonate, however, has proved effective in extinguishing fire (128,129).

Formation of Charcoal

Nearly all of the simpler gaseous compounds that are split off in the earlier stages of pyrolysis, where they escape readily, are richer in hydrogen, in oxygen, or in both, than the original cellulose or lignin. The nonvolatile residue therefore becomes enriched in carbon. Above 300° (13) or 400° C. (9, 19), the carbonaceous residue assumes a hexagonal graphitic network in which the carbon-to-carbon bonds are unbreakable by pyrolysis alone to temperatures beyond 3000° C. Such primary charcoal perhaps retains many of the carbon-to-carbon bonds originally present in the cellulose and lignin.

The more complex tarry products of pyrolysis, which escape less readily from the solid residue, undergo further strongly exothermic (59) pyrolysis that likewise leaves a more highly carbonaceous residue (39,65) and adds a secondary charcoal or tar coke (59) to the primary charcoal first formed. The extent to which tars are converted to secondary charcoal presumably depends largely on the length of time during which they remain in the solid residue (59).

The charcoal formed up to the time of completion of active pyrolysis and cessation of rapid production of gases and liquids still retains some hydrogen and oxygen. On heating to still higher temperatures, it slowly gives off volatile material, chiefly hydrogen and carbon monoxide, and the density increases up to 800° or 1000° C. (33, 59, 87, 101). Commercial charcoal commonly contains about 14 percent volatile matter (34).

Both the available data for pyrolysis of wood and the speculations about the possible pyrolytic reactions of wood components indicate that the relative yields of gases, tars, and charcoal and the proportions of flammable and nonflammable gaseous products are subject to wide variations, and may be directed by suitable catalysts or treatments. In general it is desirable, for fire resistance, to direct pyrolysis toward maximum production of charcoal, minimum production of tars, and the highest possible proportions of water, carbon dioxide, and highly oxygenated substances in the volatile products. A speeding up of the earlier, relatively slow, and less drastic part of the pyrolysis would work toward these ends, provided that deterioration of the wood did not begin within the range of temperature in which wood is customarily used. During the slower, cooler portion of the pyrolysis range, hydrolysis and dehydration reactions can proceed in more orderly fashion to denude the still macromolecular cellulose and lignin fragments of hydrogen and oxygen and of substituent and side-chain groups. Thus there will be less disruption of carbon-to-carbon bonds in glucosan and aromatic rings, leaving time for the carbon residues to condense into charcoal. The later, fast pyrolysis at higher temperatures proceeds much more violently, with more disorderly disruption of ring and chain structures to form tars and more highly hydrogenated gases, and with less condensation of carbon to form charcoal.

Theories of Flameproofing

Herodotus (45) wrote that the ancient Egyptians steeped wood in alum solution to impart resistance to fire. In the days of the Roman Empire, Remans soaked wood in vinegar and alum (32, 48, 135) or coated it with clay, lime, and loam, probably in an organic binder (32, 111, 135). In 1638 Nikolas Sabbattini recommended paint containing clay or gypsum for Italian theaters (111), and in 1820 Fuchs painted wood in the Munich Theater with sodium silicate (27, 113). In 1735 Jonathan Wild received a patent in England for a treatment with alum, ferrous sulfate, and borax (111). Gay-Lussac (31) in 1821, at the request of Louis XVIII of France, tried many treatments for flameproofing cellulosic fabrics and recommended ammonium phosphate, a mixture of ammonium phosphate and ammonium chloride, or a mixture of ammonium chloride and borax.

Thus our best chemicals for impregnating wood for fire resistance are more than a century old. Meantime long lists of chemicals, as many as 400 in a single study (125), have been tested empirically (49, 73, 104, 122, 123, 128, 133, 136) without significant improvement as far as treatment of wood is concerned, except perhaps for the discovery that boric acid, when added to borax, imparts resistance to afterglow (60).

Since flaming combustion and glowing combustion occur at different times and places and by distinctly differing mechanisms, they may be expected to differ in the means by which they may be controlled. Effective flameproofing agents may fail to retard glow and vice versa. They must therefore be considered separately. Flaming occurs earlier than glowing, progresses more rapidly, and is more important in the spread of fire.

Theories of flameproofing may be classified as coating theories, thermal theories, gas theories, or chemical theories (71). The theories, however, are by no means mutually exclusive because two or more of them may be, and probably are, operative in a given case.

1. Coating Theories

One of two theories advanced in 1821 by Gay- Lussac (31), and still current, (4, 20, 23, 36, 38, 48, 72, 98, 104, 114, 129) holds that escape of volatile combustion products from the wood and access of oxygen to the wood can be prevented by treatment with chemicals that melt and coat the wood fibers with a liquid or glassy layer before the temperature of active pyrolysis is reached. Mixtures of borax and boric acid may act in that way, although either component alone leaves a discontinuous, crystalline deposit rather than a glaze on the fibers (104).

Melts that form foams that are stable at pyrolytic temperatures (98) may be more effective than glazes. The foam serves as a barrier to air and flame, provides thermal insulation, and entraps volatile tars. Retention of the tars encourages their secondary pyrolysis to char, thereby reducing the volume of volatile combustibles. Perhaps most effective would be a mixture of components, one of which melts near 200° C. and evolves nonflammable gases such as water, carbon dioxide, ammonia, or sulfur dioxide, and another that melts just before active pyrolysis begins, producing a foam that remains stable up to 500° C. Coppick (20) reports a fairly close parallel between the height of foam produced by 5 grams of certain flame retardants when heated for 5 minutes at 450° to 500° C. in a l-inch test tube, and the effectiveness of the retardants for cotton cloth as measured by the "45° microburner test" (71). The data appear in table 3.

The coating theory does not account for the action of all flame retardants that are known to be effective because such useful materials as the ammonium phosphates, ammonium sulfamate, and the ammonium halides have negligible foaming tendencies. The published reports, however, do not seem to have considered the possibility that a suitable impregnant of low melting point might become foamed by the gases evolved in the earlier stages of wood pyrolysis. Perhaps Coppick's test for foaming tendency should be made with a disk of wood under the charge of chemical in the test tube. Further, it apparently has escaped notice that the tars formed in the pyrolysis of untreated wood readily make foam that is stable to high temperatures. Klason (59) observed that the secondary pyrolysis of the tars formed in the primary stage of pyrolysis produced a large volume of foam, beginning at 275° C. Once formed in the outer zone of the wood, such foam should have many of the same properties of insulation and entrapment of tars, which will be evolved subsequently, as are claimed for foaming fire retardants.

One promising new fire retardant has reportedly been developed in Germany by the I. G. Farben Company. The material can be brushed or sprayed on the surface of wood, sinks into the wood far enough to effectively disappear, but intumesces tremendously when flame strikes, thereby insulating the wood.

Complete impregnation or even very deep penetration of the flame retardant should be unnecessary for operation of the coating theory. A glaze or foam of moderate thickness in the surface layers or on the surface of the wood should suffice, provided that it remains stable and adherent at flame temperatures.

Indeed, fire-retardant paints or varnishes are confined almost entirely to the wood surface. Even the ordinary oil paints and varnishes exert some slight retardant action, although lacquers made with highly combustible nitrocellulose do not (91). The fire-retardant coatings contain retardant ingredients that may function in accordance with the thermal, gas, or possibly even the chemical theories in addition to their interposition of a barrier between air and wood to prevent access of oxygen and to hamper the escape of combustible gases. Coatings are said to serve in part by conducting heat away from an igniting source (84) and, on the contrary, to insulate the wood against heat (48). As long as the coatings remain intact, varnishes and paints that are not too highly pigmented are nearly impenetrable to gases (12) and, on dry wood, can withstand pressure beneath them in excess of 500 pounds per square inch (66) without parting from the wood. But coatings that remain hard up to the temperature of active pyrolysis of wood are inclined to crack and scale off. The most effective fire-retardant paints are those that intumesce strongly somewhat before the wood underneath reaches the temperature or active pyrolysis, producing a voluminous foam that remains stable and relatively

noncombustible up to flame temperatures. A commercial paint of that type was recently tested in the tunnel furnace at the Forest Products Laboratory; a coating 7 roils thick intumesced to an adherent layer of carbonaceous foam more than one inch thick. The foam burned exceedingly slowly where directly in contact with the pilot flame and exhibited no afterglow. That the paint functioned largely by thermal insulation was evident from the very thin layer of charred wood underneath. The paint was reported to contain an organic phosphorus compound that left its phosphorus in the char after pyrolysis.

Paints and other superficial treatments are attractive for the ease with which they can be applied, even after woodwork has been erected, and for the comparatively small amount of protective material required. But if external heat is supplied long enough, pyrolysis of the wood underneath must eventually set in. Deep impregnation of the wood therefore seems to offer greater possibilities.

2. Thermal Theories

Thermal theories are of three kinds -- thermal insulation to retard the access of heat to the wood, thermal conductivity to dissipate the heat more rapidly, and thermal absorption to reduce the amount of heat available for pyrolysis.

(a) Thermal Insulation. -- Thermal insulation by coatings, glazes, and foams has already been mentioned as part of the coating theories. Untreated wood in pieces that are not too small insulates itself thermally by forming a layer of charcoal on the surface to retard the penetration of heat (84, 113, 114). Little consideration seems to have been given to the possibility of further improving the insulating effect by treatments to cause intumescence of the charcoal layer to increase its thickness and its insulating value; however, Metz (84) reports that an unusually loose layer of charcoal is formed by salts, such as potassium carbonate, cyanide, or acetate, which presumably release strong alkali at pyrolysis temperatures. In some tests at the Forest Products Laboratory, great swelling of the charcoal on wood treated with potassium carbonate has been observed.

(b) Thermal Conductivity. -- At the opposite pole is a theory that combustion may be prevented by increasing the thermal conductivity of wood sufficiently for heat to be dissipated faster than it is supplied by an igniting source (20, 38, 84, 114). The theory obvioulsy is derived from the funtioning of the Davy Safty Lamp. No experimental evidence has been advanced to support the hypothesis. Presumably, wood's low conductivity would have to be raised to a level approaching that of metals to dissipate heat fast enough for the purpose.

A crude test was made at the Forest Products Laboratory with some small specimens of untreated wood and of similar wood completely impregnated with a metal alloy that would melt at 105° C. Both the untreated and the impregnated wood were heated at the center of one face with a tiny flame from a Bunsen burner. The rate of rise of temperature was observed with a thermocouple in contact with the unheated side, immediately opposite the point of application of the Bunsen flame. Rise of temperature was slower over the metal-impregnated specimen until the metal melted, after which the rate of rise was essentially the same for treated and untreated specimens until the point of exothermic Pyrolysis was reached. The exothermic point occurred at the same temperature and at nearly the same time for both treated and untreated specimens. The untreated specimen then quickly burst into flame, whereas the metal-impregnated specimen merely began to smoke and then charred without flaming. Although impregnation with metal effectively prevented flaming combustion, it clearly did so by a mechanism other than dissipation of heat by conduction. Peschek (98) reported that metal-impregnated wood evolves no combustible gases on heating.

(c) Thermal Absorption. -- The third of the thermal theories postulates decomposition or change of state of the retardant chemical to absorb enough heat to keep the temperature of the wood from reaching the ignition point (20, 23, 36, 38, 48, 72). The best example of the theory perhaps is the poor combustibility of wet wood. Few substances, however, have endothermic heats of transition or of decomposition comparable to the heat of vaporization of water. Even with water a high retention of retardant is required for good effectiveness. The protection is at best temporary because exhaustion of the endothermic evaporation leaves the wood subject to combustion as usual. Study of the thermal behavior of a large number of substances failed to reveal any connection between effectiveness as fire retardants and ability to absorb heat (20).

Borax, a good retardant, contains 10 molecules of water of crystallization, which is 89.5 percent by weight of the anhydrous chemical. On heating, it begins to lose the water of crystallization at 80° C. and loses all of it at 200° C. The heat of hydration is 34.1 kilocalories per mole (82). The "melting point" of the remaining salt is given variously as 561° to 878° C. If borax prevents combustion wholly by absorbing heat by its dehydration, enough of the chemical must be present to offset, or nearly offset, the heat liberated by pyrolysis of the wood above the exothermic point. Klason (59) calculated the heat liberated as 96.7 kilocalories per kilogram for 8-hour pyrolysis and as 169.2 kilocalories per kilogram for 14-day pyrolysis of birch at atmospheric pressure. For a cubic foot or about 20 kilograms of birch, the heat liberated would be 1,934 to 3,384 kilocalories. To offset it, from 56.7 to 99.5 moles or 25.2 to 44.3 pounds of borax per cubic foot, calculated as anhydrous salt, would be required. Yet borax is effective as a fire retardant in retentions of 3 to 6 pounds per cubic foot (49). Absorption of heat by dehydration, therefore, can account in no more than a minor part for its effectiveness.

Schlegel ([113]) tried to establish a parallel between the effectiveness of 30 fire-retardant salts and their "molecular heat capacity" between room temperature and the temperature of combustion (taken as about 800° C.); or, if the salts dissociate, to establish the sum of the "heat capacities" of the components that exist at combustion temperature. Since the specific heats of the salts at high temperatures are not known reliably, the considerations remain highly speculative and unconvincing ([84]).[3]

Absorption of heat should prove most beneficial if it occurs at the exposed surface of the wood where the temperature of exothermal pyrolysis is reached soonest. It is conceivable that fire-retardant paints might act partly in this way. As yet, however, there seem to be no data on the thermal changes that occur in such paints.

Although the thermal theories no doubt play minor parts in fire retardance, they do not seem to offer much prospect of providing sustained protection at moderate retentions.

3. Gas Theories

There are two gas theories -- that of dilution of the combustible gases of pyrolysis with noncombustible gas es from the retardant, and that of catalytic inhibition of flaming by free radicals capable of breaking the reaction chains of normal gaseous combustion.

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[3] Schlegel's work is of interest for his novel adaptation of the Forest Products Laboratory fire-tube test. The apparatus was scaled down to accommodate test specimens 1.0 by 1.0 by 10 centimeters in size. In place of the weight loss after combustion has ended, significance was attached to the average rate of loss in weight during the time taken for the temperature at the top of the chimney to reach its maximum. The effectiveness, w, of a treatment with x gram molecules of a given salt per kilogram of wood was taken as the difference between the rate of loss of untreated wood, y_0, and the rate of loss of the treated wood; that is, $w = y_0 - y$. For relatively heavy treatments, such as 1 gram molecule or more per kilogram of wood, a "law of mass action" was disclosed whereby $x = a^w$ in which a was a determinative constant for the particular salt. From this the "specific effectiveness" of a salt was defined as $1/\log a$. For light treatments the "law of mass action" usually failed to apply; in fact, 15 of the salts tested actually increased the rate of loss in weight in very light treatments even though some of them -- notably ammonium bromide, lithium chloride, and potassium carbonate -- were very effective in heavy treatments. Coppick ([20]) similarly reported accelerated combustion of cotton fabric with very light treatments of some salts that were very effective in heavier treatments.

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(a) Dilution with Noncombustible Gas. -- In addition to his coating theory, Gay-Lussac (31) offered a second theory to the effect that noncombustible gases evolved by decomposition of the fire retardant will dilute the combustible gases from the pyrolyzed wood sufficiently to render the mixture nonflammable in air. The theory still finds supporters (4,20,23,36,38,48,72,84,98,113, 114). In a variation of the theory, the diluting gases are thought to form a blanketing layer to exclude oxygen from contact with the combustible pyrolysis gases until the latter have escaped from the zone of high temperature (20,79).

The gases usually considered effective diluents are water, carbon dioxide, ammonia, sulfur dioxide, and hydrogen chloride. One or more of them may come from decomposition of highly hydrated salts, from alkali carbonates or bicarbonates, from ammonium halides, phosphates, and sulfates, from chlorides of zinc, calcium, and magnesium, or from ammonium sulfamate. The retardant must not decompose at temperatures of ordinary use of wood, but it should yield its diluting gases rapidly at a temperature slightly below that at which active pyrolysis of wood sets in, perhaps a little below 270° C. If, as will appear in the discussion of chemical theories, the retardant lowers the temperature of active pyrolysis of wood, the retardant should yield its gases rapidly at a correspondingly lower temperature.

The gas dilution theory has been criticized adversely (20,104,129) on the ground that too little noncombustible gas is liberated by any practicable retention of fire retardant to prevent flaming of the large quantity of combustible gases and vapors formed by pyrolysis of wood. The criticism, however, may not be entirely fair because the gases evolved by pyrolysis of wood are already diluted with nonflammable components. Thus, rough calculation from Klason's data (58) for 8-hour pyrolysis of dry birch at atmospheric pressure indicates that 1 cubic foot of wood yields 590 cubic feet of gases and vapors at 300° C.; of this amount, 380 cubic feet is steam, 75 cubic feet is carbon dioxide, and only 135 cubic feet, or 22.9 percent by volume, consists of flammable gases and vapors. Martin (79), as already mentioned, comments that such a gaseous mixture should be nonflammable. Mixtures in all proportions of carbon monoxide with air are rendered nonflammable by addition of 54 percent of steam or of 52 percent of carbon dioxide (21). The flammability of the pyrolytic gases from wood therefore comes largely from the mist of tar carried with them. If the 1 cubic foot of dry birch in Klason's work was impregnated with 6 pounds of borax, calculated on the anhydrous basis, and if the borax did not otherwise alter the pyrolysis of wood, the 10 molecules of water of crystallization in the borax would add about 225 cubic feet of steam to the gaseous products evolved. This, together with the 380 cubic feet of steam and 75 cubic feet of carbon dioxide from the wood, might well serve to suppress the flammability of the tar mist.

(b) Chain-Breaking Inhibitors. -- A recent theory relies on the inhibition of flaming of the gaseous products by a suitable gaseous catalyst released at pyrolysis temperatures by decomposition of a fire-retardant chemical. The catalysts usually proposed are the halogens and halogen acids, among which the effectiveness has been found to increase in the order of fluorine, chlorine, bromine, and iodine (29, 36, 109, 115). Thus, addition of 6.2 percent of methyl bromide or 2.0 percent of carbon tetrachloride to carbon monoxide makes a mixture that is nonflammable in air in all proportions, whereas additions of 54 percent of water vapor or 52 percent of carbon dioxide are required to accomplish the same purpose by dilution (21). Combustion in flames is believed to proceed by branching chain reactions among free radicals (119). Diluents such as water vapor absorb heat and reduce the frequency of collisions between reactive molecules or radicals, but do not alter the chain reactions otherwise. Inhibitors such as the halogens break the reaction chains. At flame temperatures the halogens decompose to halogen atoms that combine with radicals essential to the combustion process, after which the new combination yields a stable molecule, or at least a less reactive radical, and regenerates the halogen to repeat the process (109). Thus, if such free radicals as HCO and OH are active in propagating combustion, the presence of a relatively small amount of bromine may destroy them as follows:

$$HCO + Br \longrightarrow HBr + CO$$

$$OH + HBr \longrightarrow Br + H_2O$$
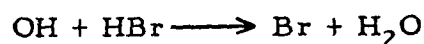
Regeneration of the inhibitor permits it to quench flames in much smaller amounts than are necessary with diluents.

Halogen-containing retardants must be stable at temperatures of ordinary use of wood because the halogens and halogen acids attack wood and impair its strength. But the retardant must decompose at or slightly before active pyrolysis of wood begins in order to supply the inhibitor when it is needed. Of course the retardant itself should be incombustible.

4. Chemical Theories

The preceding discussion of the coating, thermal, and gas theories largely ignored any effect exerted by fire retardants on the course of pyrolysis of the wood itself. The chemical theories, on the other hand, aim to change the pyrolysis of wood in a favorable direction. It has already been pointed out that the yields of gases, tars, and charcoal from untreated wood are profoundly altered by changes in the temperature, pressure, or rate at which pyrolysis takes place. That fire retardants likewise alter wood pyrolysis is only to be expected.

Effective fire retardants significantly lower the temperature at which rapid pyrolysis of wood, with production of char, sets in (16, 85, 94) and raise the temperaturc at which the pyrolysis becomes exothermic (84, 94, 134). The quantity of charcoal produced is materially increased (7, 14, 16, 48, 105, 129, 134). The increase in charcoal must result in decreased production of tar or of gases (14, 48, 105, 123, 134) or of both (129), but the published ports fail to reveal quantitative data from which product balances can be calculated. Much more work, directed toward the theory of fire-retardant action, has been done with cellulose in the form of filter paper (122, 125) cotton textiles (15, 20, 36, 38, 69, 78, 97, 104, 114, 115) than wood. There should, however, be a close parallel between cellulose and wood (114).

Ramsbottom (104) reports the data of table 4 to show how fire retardants lower the charring temperature of cotton fabrics. But marked lowering of the char-ring temperature does not always indicate a corresponding increase in the ate of decomposition of the cellulose (125). The exothermic point in pyrolysis of wood is said to be raised from 300° 500° C. by treatment with fire re-tardants (134). For the effect of chemicals on the yield of charcoal in com-bustion of cotton fabric, Rams bottom (104) gives the data of table 5. Effective retardants may more than double the yield of charcoal, whereas ineffective chemicals, such as sodium chloride, may decrease it. But when pyrolyzed in vacuo at temperatures below 300° C. , impregnation of cotton cellulose with sodium chloride has been found to increase the yield of charcoal (78).

The increase in yield of charcoal by fire retardants apparently is accomplished chiefly at the expense of tar production. Coppick (20) reported the data of table 6 on yields of dry tar, aqueous condensate, and dry gas for cotton fabric treated with chemicals of varying effectiveness, as measured by a test for duration of afterflaming (71). There, was a close parallel between reduction in flammability and reduction in tar production. Flammability practically ceased when the tar production fell below about 3 milligrams per square centi-meter of fabric, which was a little less than one-fourth the amount of tar from untreated fabric. Borax-boric acid mixture attained that condition and borax alone nearly attained it when the fabric contained about 5 percent of chemical. Sodium chloride, even at 33.7 percent retention, failed to reduce flaming or to reach such a low level of tar production, although it did reduce tar forma-tions substantially. Table 7 from Gulledge and Seidel (38) is of interest in this connection because it reports yields of both char and tar. Nearly all ob-servers of either wood or cellulose fire tests agree that fire retardants sig-nificantly diminish the formation of tar; the exception is Yoshimura and co-workers (140), who seem to report increases in tar formation by zinc chloride, calcium chloride, phosphorus pentoxide, and sodium hydroxide.

Table 6 indicates that added chemicals, whether good or poor retardants, in-crease the amounts of aqueous condensate and dry gas formed on combustion

of fabric, and do not alter appreciably the composition of the dry gas. Ammonium phosphate and ammonium sulfamate affected the production of gas much like the other chemicals (20). Although added chemicals increased the amount of dry gas without appreciable change in ratio of combustible gases to carbon dioxide, it must be remembered that the gas phase arising from the burning fabric included the tars and the aqueous condensate, which was chiefly water. Since 1 milligram of steam occupies more than 1.25 cubic centimeters, the gas phase was in fact greatly diluted with steam and impoverished in the highly flammable tars. Moreover, with effective retardants the gases and vapors begin to come off more rapidly at lower temperatures than with untreated fabric, and have more opportunity to escape before taking fire (36, 114).

It appears, therefore, that the effective fire retardants act chiefly by directing the decomposition of cellulosic materials, presumably including wood, toward the formation of much less tar and more water and charcoal, and by starting the decomposition at lower temperatures. Moreover, the retardants probably raise the temperature at which the decomposition becomes exothermic. The outstandingly important criterion of flammability seems to be the production of tars. The quantity of fixed gases and their ratio of combustible to incombustible components seems to be less important.

Possible Mechanisms of Chemical Action of Retardants

The effect of fire retardants on the charring temperature, the yield of products, and the exothermic point suggests that wood is attacked chemically and partly decomposed before combustion can begin. The majority of retardants impair the strength of cotton fabric to some extent even at ordinary or only slightly elevated temperatures (20), and some materials that would otherwise be effective retardants cannot be used because they weaken wood or cotton too seriously (104). Desirable retardants should be harmless to wood at the temperatures of ordinary use, but should themselves decompose or otherwise generate the effective reagent at a temperature above that of common use but well below that of combustion for untreated wood.

Hydrophilic Nature of the Best Retardants

The highly effective inorganic fire retardants are all soluble in water. Although such volubility facilitates application, it has the disadvantage of loss of chemical by leaching if the treated wood is exposed to the weather. Efforts have been made to precipitate insoluble retardants in wood by double treatments (103, 127). The results, however, have been inferior to those obtainable

with water-soluble substances. Such success as there was may have been due more to soluble byproducts or excess reagent left in the wood than to the insoluble precipitate. In cotton fabric the insoluble precipitates can be formed and the soluble products and reagents removed easily by washing. Extensive tests made in that way (104) revealed no insoluble substances comparable in effectiveness to the better water-soluble salts. Ferric oxide, stannic oxide, lead monoxide, manganese dioxide, and ferric chromate were moderately effective against flaming but usually stimulated glowing. Some of the insoluble compounds thought to have been formed to advantage in wood (127), such as magnesium ammonium phosphate, proved completely ineffective.

No one seems to have pointed out that the poor results with insoluble substances may be of fundamental significance. It strongly confirms the dominance of chemical over purely physical mechanisms in the theory of fire-retardant action. Effective retardants perhaps must have those hydrophilic properties that lead to volubility in water if they are to direct the pyrolysis of cellulose and wood toward maximum production of charcoal and water, rather than of tars and combustible gases. The consideration draws attention to possible reactions at the hydroxyl groups of cellulose and lignin.

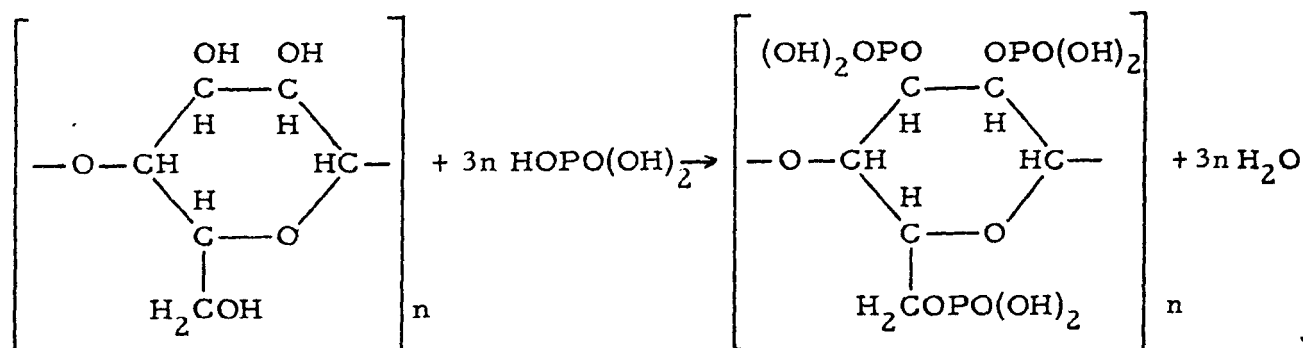## Effectiveness of Strong Acids and Bases

Both strong acids and strong bases attack cellulose. It has been observed repeatedly that salts that may be expected to dissociate to form acids or bases on heating usually lower charring temperatures and impart good fire resistance to wood (6, 84, 117) and to cotton fabric (15, 18, 20, 69, 104, 114). Most of the effective retardants are salts, either of strong acids—with weak bases, such as ammonium chloride or zinc chloride, or of strong bases with weak acids, such as borax or potassium carbonate. Salts of strong acids with strong bases, such as sodium chloride, are usually ineffective. Phosphoric acid and the ammonium phosphates are effective, as is sodium hydroxide also, but trisodium phosphate is much less effective and sodium dihydrogen phosphate and disodium hydrogen phosphate are of little value. (Of course phosphoric acid and sodium hydroxide would be impracticable because they attack wood at room temperature.) Aluminum sulfate is a good retardant, whereas sodium sulfate is not. On the other hand, sodium carbonate is a fairly good retardant and sodium tungstate is definitely good, whereas ammonium carbonate and ammonium tungstate are not.

In addition to the strong acids and bases, oxidizing agents such as potassium nitrate, metallic chromates, selenium, potassium permanganate, and potassium thiocyanate degrade cellulose and are of some value as fire retardants (20, 104, 114, 125), although for the most part they are impracticable. Oxidized cellulose begins to pyrolyze rapidly at relatively low temperatures and leaves much charcoal and very little tar (78).
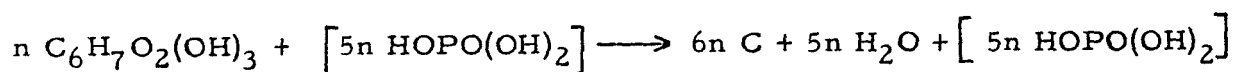
There is reasonably satisfactory agreement among various investigators about the relative merits of the water-soluble inorganic salts for flameproofing wood or cotton fabric (49, 97, 104, 113, 122, 123).

Dehydrating Mechanism of Acids

Serebrennikov (117) held that strong acids, such as sulfuric and phosphoric, encourage pyrolysis to carbon and water by their reactivity with hydroxyl groups and by the avidity with which they absorb water. Phosphoric acid, for example, may react first with the hydroxyl groups of glucosan units in cellulose thus:

$$
\left[
\begin{array}{c}
\text{OH} \quad \text{OH} \\
\text{C}\!-\!\text{C} \\
\text{H} \quad \text{H} \\
-\text{O}-\text{CH} \qquad \text{HC}- \\
\text{H} \\
\text{C}\!-\!\text{O} \\
| \\
\text{H}_2\text{COH}
\end{array}
\right]_n
+ 3n\ \text{HOPO(OH)}_2 \rightarrow
\left[
\begin{array}{c}
\text{(OH)}_2\text{OPO} \quad \text{OPO(OH)}_2 \\
\text{C}\!-\!\text{C} \\
\text{H} \quad \text{H} \\
-\text{O}-\text{CH} \qquad \text{HC}- \\
\text{H} \\
\text{C}\!-\!\text{O} \\
| \\
\text{H}_2\text{COPO(OH)}_2
\end{array}
\right]_n
+ 3n\ \text{H}_2\text{O}
$$

Presence of the phosphate groups then prevents pyrolysis by way of polyhydroxy aldehydes, glycolic aldehyde, and ketones, as previously described for cellulose. Instead, the acid in conjunction with part of the water formed by the initial reaction may be expected to cause hydrolysis at the linkages between glucosan units, exposing two additional hydroxyl groups for reaction with the acid. Finally the HCOPO(OH)$_2$ groups may pyrolyze to regenerate the phosphoric acid and leave carbon and water. The overall reaction would then be:

$$
n\ \text{C}_6\text{H}_7\text{O}_2\text{(OH)}_3 + \left[5n\ \text{HOPO(OH)}_2\right] \longrightarrow 6n\ \text{C} + 5n\ \text{H}_2\text{O} + \left[5n\ \text{HOPO(OH)}_2\right]
$$

The fact that cellulose acetate cannot be fireproofed with the retardants used for flameproofing cotton (114) lends support to the theory. Since the hydroxyl groups of the glucosan units are already bound to acetyl groups, the initial reaction with inorganic acid is precluded. Decomposition does not begin until the temperature is high enough for the normal pyrolysis of untreated cellulose to set in. The pyrolysis then follows essentially the same course as that described for cellulose except that acetic acid entirely replaces the water formed in pyrolysis of cellulose (78). At higher temperatures the acetic acid yields carbon dioxide and methane, the latter being flammable.

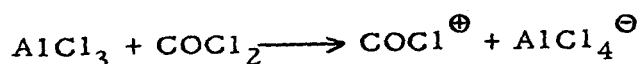## Lewis Acids and Bases

Several authors (15, 36, 114, 115) have pointed out that the theory of catalytic de:hydration acquires more general application when acids and bases are defined in accordance with the Lewis electronic theory (74). Compounds that contain an element capable of accepting electrons to fill out its outer shell are Lewis acids, and those compounds with an element having a lone electron pair to share are Lewis bases. In water, the hydrogen ions dissociated from ordinary acids form hydronium ions:

$$H^{\oplus} + H:\overset{..}{\underset{..}{O}}:H \longrightarrow \left[H:\overset{\overset{\textstyle H}{|}}{\underset{..}{O}}:H \right]^{\oplus}$$
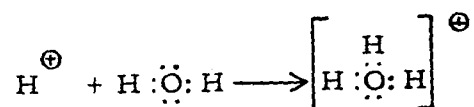
But the Lewis acids and bases include compounds that do not dissociate hydrogen or hydroxyl ions. Thus, boron trichloride as a Lewis acid neutralizes triethyl amine:
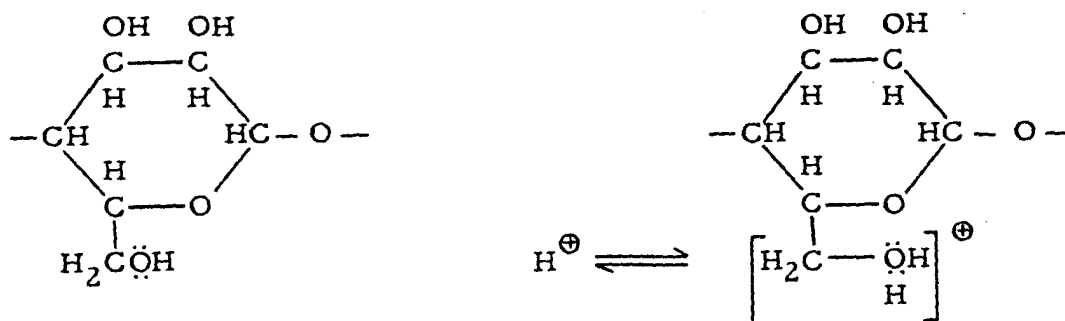
$$\begin{array}{ccc}
\overset{\textstyle Cl}{\underset{\textstyle Cl}{Cl-B}} & + & \overset{\textstyle Et}{\underset{\textstyle Et}{:N-Et}}
\end{array} \longrightarrow
\begin{array}{c}
\overset{\textstyle Cl}{\underset{\textstyle Cl}{Cl-B}} \cdot : \overset{\textstyle Et}{\underset{\textstyle Et}{N-Et}}
\end{array}$$
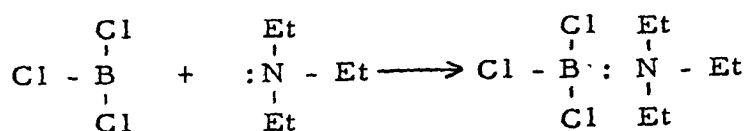
and aluminum chloride reacts with phosgene:

$$AlCl_3 + COCl_2 \longrightarrow COCl^{\oplus} + AlCl_4^{\ominus}$$

When such processes involve carbon atoms of organic compounds, carbonium ions or carbanions are formed.

Acids catalyze dehydration of a glucosan unit in cellulose in some such manner as the following (114):

Addition of the proton to the oxygen atom of a hydroxyl group disturbs the electronic system by drawing the pair of electrons between carbon and oxygen closer to the oxygen, making it easy for water to split off and leave a carbonium ion:

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(2)

$$\left[H_2C\!-\!\overset{..}{\underset{H}{O}}H \right]^{\oplus} \;\rightleftharpoons\; H_2O + \; H_2C^{\oplus}$$
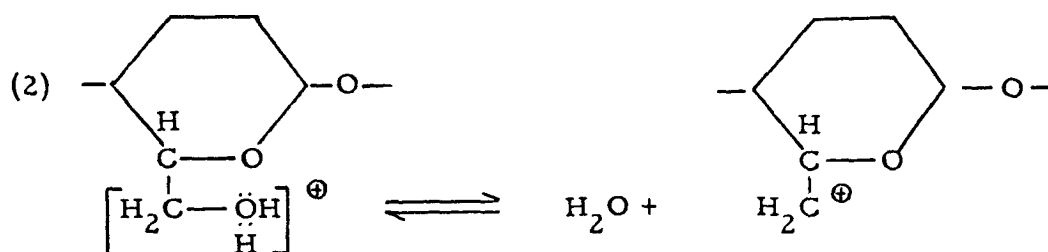
The carbonium ion is unstable and rearranges electronically to regenerate the proton, which can then repeat the process at another electron-rich point:
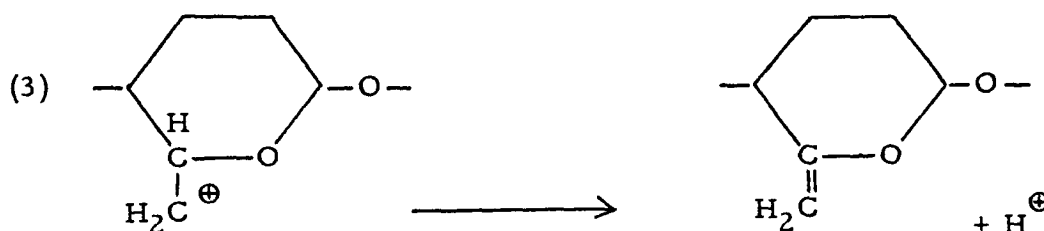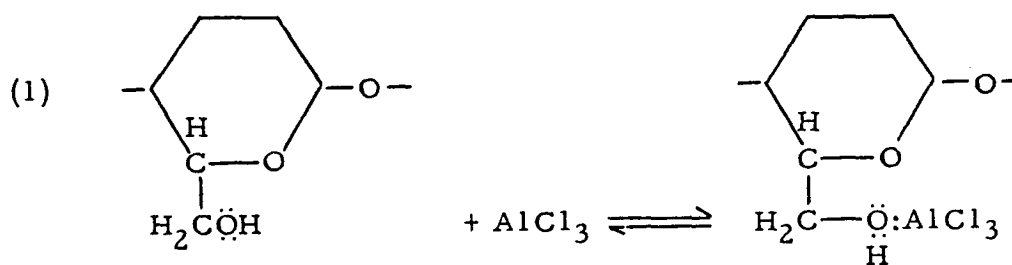
(3)

$$H_2C^{\oplus} \;\longrightarrow\; H_2C \;\; + H^{\oplus}$$

Elimination of water takes place by removal of a hydroxyl group from one carbon atom and a hydrogen atom from the adjacent carbon atom, leaving the carbon atoms joined by a double bond. Remembering that acids also catalyze hydrolytic splitting apart of the glucosan units, it is easy to see how repetition or concurrent operation of the process strips off the hydrogen atoms and hydroxyl groups and perhaps the oxygen in the ring without breaking carbon-to-carbon bonds.

Dehydration through carbonium ions is effected similarly by such Lewis acids as aluminum chloride, aluminum oxide, phosphoric oxides, and stannic oxide. Thus (114):

(1)

$$H_2C\overset{..}{O}H \;\; + AlCl_3 \;\rightleftharpoons\; H_2C\!-\!\underset{H}{\overset{..}{O}}{:}AlCl_3$$

(2)

$$H_2C\overset{\oplus}{}\ \rightleftharpoons\ +\left[\overset{..}{\underset{H}{\overset{..}{O}}} - AlCl_3\right]^{\ominus}$$

(3)

$$+\ H^{\oplus}$$

(4) $\quad H^{\oplus} + \left[\overset{..}{\underset{H}{\overset{..}{O}}} - AlCl_3\right]^{\ominus} \longrightarrow H_2O + AlCl_3$
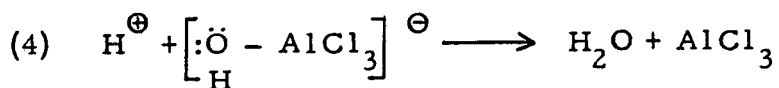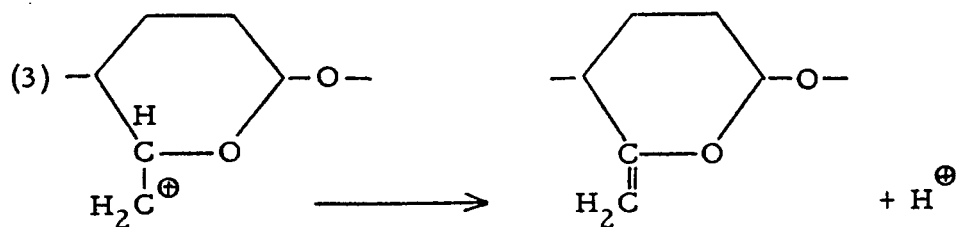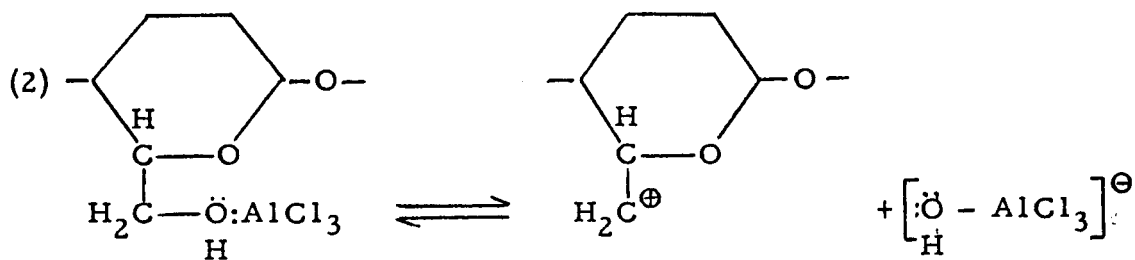
These considerations elaborate Serebrennikov's picture of the catalysis of pyrolytic dehydration of cellulose by acids and extend it to known fire retardants that are not acids in the ordinary sense. Flameproofing by bases such as sodium hydroxide or by Lewis bases can be explained by a similar mechanism involving carbanions (114):

(1) $\quad OH^{\ominus} +$

$\rightleftharpoons H_2O +$

(2)

$\longrightarrow$

$+\ OH^{\ominus}$
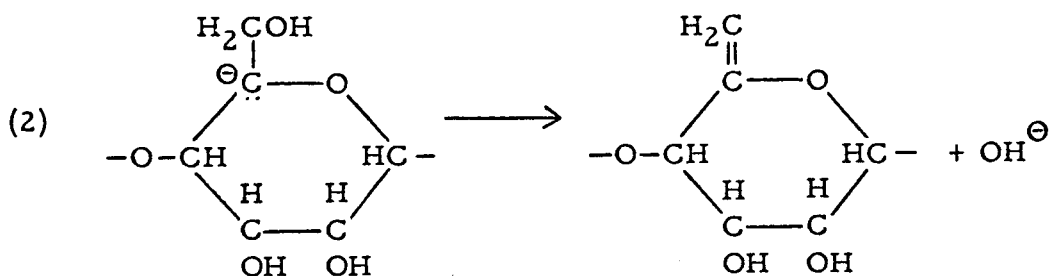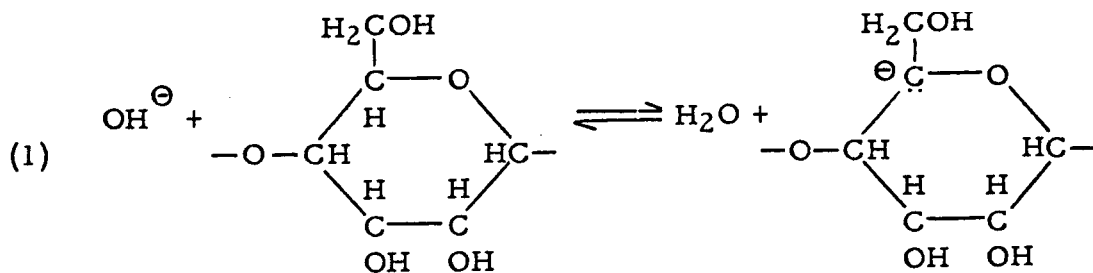
Hydrozen Bonding Action

Another approach to understanding the mechanism by which fire retardants in. crease the yield of charcoal is attributed to W. A. Sisson by Coppick (20):

"The majority of the effective flame-retarding chemicals contain group-
ings that are active in hydrogen-bridging processes. The well-ordered
and relatively inactive portion of cellulose is considered to involve the
hydrogen bonding between adjacent hydroxyls, and the disordered and
active portions are characterized by the bridging of adjacent chains via
water molecules. The structural stability of the system is critically
related to these intermolecular forces and it is proposed that on con-
tact with high temperature sources the bridging media are lost owing
to the thermal activity of water at these temperatures, but that the
linkages may be maintained if a nonvolatile component of sufficient
hydrogen-bonding activity is present. The electronic configurations
that promote strong linkages of this type in the cellulose system are
$= O, - OH,$ and $- NH_2$. These groupings are particularly prevalent
in the more efficient retardants such as the phosphates, sulfates, and
sulfamates, and the theory proposes that thermal stability and the con-
fining of fragments to the solid phase is due to a great extent to the
hydrogen-bonding capacity of these compounds. It is further pointed
out that the main chemical characteristics of the strong dehydrators
and the hydrated salts effective in retardant action is their active
hydrogen-bonding power, and although they prefer to stabilize their
electronic configurations by bonding with water, in the absence of the
latter the cellulosic hydroxyl serves the same function."

The hydrogen-bonding theory is quoted by other recent workers (36, 72), but
is rejected by Schuyten, Weaver, and Reid (114) on the ground that even the
strongest hydrogen bonds have a bond energy no more than 9 to 10 kilocalories
per mole and are unlikely to exist at temperatures of 400° to 500° C. Coppick
(20), however, suggests that the di- and tri-functionality of the phosphates,
sulfates, and sulfamates, also provide for cross linking through primary bonds
to bind fragments together in the solid phase and hamper splitting off of vola-
tile chain fragments. Moreover, such three-dimensional effect may proceed
also by polymerization or condensation of aldehydic groupings catalyzed by
the strong acid or alkali thermal dissociation products of the retardant. Simi-
larly Gulledge and Seidel (38) explain the effectiveness of a titanium oxide and
antimony oxide complex on the basis of reactivity with organic hydroxyl groups
both by primary valence and chelation.

Application to Lignin

There seem to be no published theories of the effect of fire retardants on the chemical mechanisms of the pyrolysis of the lignin component of wood. Since cellulose normally pyrolyzes at a lower temperature than lignin and perhaps the lag may be even greater in treated wood, it may be that the lignin enjoys a measure of protection by the layer of charcoal left by the cellulose. The structure of wood, which is retained for some time after pyrolysis sets in (35, 83, 130), accords with such a relation because the cavities through which gases must escape are lined with cellulose-rich walls, with the lignin-rich middle lamella sandwiched between them. Presence of the cellulose char may trap any tars from the lignin and favor their secondary pyrolysis. Freshly formed carbon may well be expected to exert profound catalytic effects on subsequent pyrolysis of lignin. Lignin normally forms much more char but perhaps a little less tar, and hence may contribute less to flammability than cellulose, even without fire-retardant treatment.

The more or less orderly action of Lewis acids and bases at hydroxyl groups leading to dehydration to carbon and water, as postulated for cellulose, cannot apply without modification to lignin with its irregularly varied structure. In place of the 2 to 1 ratio of hydrogen to oxygen in cellulose, the ratio in lignin is more than 3 to 1. Nevertheless lignin presents numerous alcoholic hydroxyl groups for reactions similar to those attributed to cellulose. The analogous reaction at phenolic groups would form the carbonium ion

$$
\begin{array}{c}
\quad\ \ \overset{H}{C}\!=\!\overset{H}{C} \\
HC\qquad\ \overset{\oplus}{C} \\
\quad\ \ \underset{H}{C}\!-\!\underset{H}{C}
\end{array}
$$
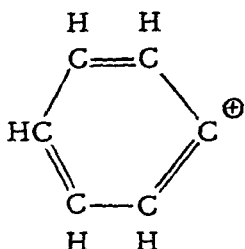
This could hardly reach a stable configuration without breaking the aromatic ring and shifting hydrogen, for example, to

$$HC \equiv C - CH = CH - C \equiv CH$$

which would still be unstable and break further into carbon and less unsaturated hydrocarbons. The methoxy groups of lignin are believed to split off as methyl alcohol in normal pyrolysis and presumably would do so even more readily in the presence of Lewis acids. Presence of Lewis acids almost certainly would hamper the phenol-aldehyde reaction and similar condensation reactions among primary pyrolysis products to which formation of tar is largely attributed. On

the whole it is reasonable to suppose that fire retardants lower the tempera-
ture of pyrolysis of lignin, increase the production of carbon and water, and
diminish the formation of tars much as they do with cellulose. For the ex.
cess hydrogen in lignin beyond two atoms of hydrogen for one of oxygen, it is
to be remembered that charcoal is far from pure carbon. Charcoal normally
retains at least 14 percent of material volatile at much higher temperatures
 (34), more than 90 percent of which is hydrogen   (42).

Theories of Glow Prevention

The process of combustion of charcoal, the solid phase in the pyrolysis prod-
ucts of wood, is essentially independent of the process of flaming combustion
of the gaseous and liquid phases. Such independence was well demonstrated
by Fons (26), who exposed slender dowels of ponderosa pine in an electric fur-
nace at different temperatures. At temperatures somewhat below 232° C. the
wood was reduced to charcoal without either flame or glow; between 232° and
443° to 463° C. (according to diameter of specimen) the wood charred and was
then consumed by glow without flame; above 463° C. the wood flamed until
evolution of volatile combustibles ceased, and then glowed until the charcoal
was consumed.

It therefore is not surprising that the effect of any one chemical on flaming
may differ markedly from its effect on glowing. In tests of many chemicals
at the Forest Products Laboratory (49), only the ammonium phosphates and
phosphoric acid proved highly effective against both flaming and glowing. So-
dium molybdate, which was highly effective against flaming, and chromic acid
and the chlorides of chromium, manganese, cobalt and copper, which were
only a little less effective against flaming, all made wood glow more intensely
than untreated wood. Such excellent flame inhibitors as borax and sodium ar-
senate and such good inhibitors as aluminum chloride and ammonium sulfate,
as well as poor inhibitors such as sodium chloride, had no noticeable effect
on glowing. On the other hand boric acid, ammonium borate, and sodium am-
monium phosphate were excellent glow inhibitors but were poor or only moder-
ate inhibitors of flame. Similar findings are reported for cotton fabric (20,
69, 72, 104).

Effective retardants for glow are much less numerous than the effective re-
tardants for flame. In wood the good inhibitors of glow are chiefly the ammoni-
urn phosphates, phosphoric acid, boric acid, or substances that yield phosphoric
or boric acid at pyrolysis temperatures. It is of interest that the glowing of
carbon deposits in gasoline engines is prevented by adding certain organic phos-
phorus compounds to the fuel. These compounds, such as trimethyl phosphate,

tritolyl phospfate and ditolyl phosphonate (47), yield phosphoric acid on burning. For some other compounds the reports are conflicting. Thus zinc chloride and chromium chloride are said to prevent glow in cotton yarn (97), but in wood zinc chloride was rated only slightly effective and chromium chloride was found to increase glow (49). Silica is reported as effective (38) and as ineffective (104) against glow in cotton fabric.

There are both physical and chemical theories of glow retardance.
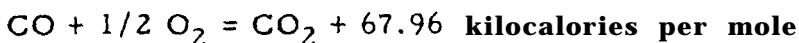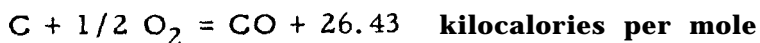
1. Physical Theories

Exclusion of oxygen from contact with the surface of hot charcoal prevents glow. Intumescent paints, provided that they remain intact at combustion temperatures, accomplish such exclusion of oxygen. One of the best intumescent paints tested at the Forest Products Laboratory, however, makes a highly carbonaceous foam; so, the question of glow prevention is merely transferred from the wood char to the paint char. The paint in question was reported to contain an organic phosphorus compound that left the phosphorus permanently in the char.

The coating theory has been advanced for some impregnated glow retardants, such as borax-boric acid mixtures, but it has been shown that there is no consistent relation between the proportions of such mixtures that form continuous coatings on char and those that are effective against glow (20, 104). Some of the best glow retardants, such as the ammonium phosphates, are not believed to form coatings.

Theories of glow prevention by the cooling effects of increased thermal conductivity or of absorption of heat by endothermal changes in the retardant are subject to the same limitations discussed previously in connection with flameproofing.

2. Chemical Theories

Glowing combustion of charcoal is similar to the combustion of coke or other pyrolyzed forms of carbon. It involves oxidation at or near the surface at temperatures of 600° to 700° C. or higher. Some (2, 72) believe that the reaction occurs in two stages:

$$C + 1/2\ O_2 = CO + 26.43 \quad \text{kilocalories per mole}$$

$$CO + 1/2\ O_2 = CO_2 + 67.96 \quad \text{kilocalories per mole}$$

Oxidation of carbon all the way to carbon dioxide evolves 94.39 kilocalories per mole. The primary reaction takes place at the interface between carbon

and air; the secondary reaction occurs in the gas phase and evolves nearly 2-1/2 times as much heat as the primary reaction. There are other theories that postulate initial formation of carbon dioxide followed by its reduction to carbon monoxide (40), simultaneous formation of the monoxide and dioxide (53), or initial pentration of oxygen into the carbon structure to form graphitic oxides that then decompose to carbon dioxide and carbon monoxide (86, 107). Detailed reviews of the theories have been published (55,107). Whatever the theory, however, the net heat liberated by the combution is determined by the ratio of CO to CO_2 in the products. The evidence indicates that effective glow retardants greatly increase the ratio of $CO:CO_2$ and thereby minimize the heat available for propagation of the oxidation. If the reaction can be directed very largely to the monoxide, the heat liberated is only 28 percent of that set free in complete conversion to the dioxide and may prove insufficient to propagate combustion.

The enormous extent to which the $CO:CO_2$ ratio can be altered by catalysts is illustrated by some tests by Arthur and Bowring (2). Wood charcoal and other forms of carbon were burned at 850° C. in a stream of dry air to which the catalysts were added in varying quantities. The conditions were such that without catalyst the carbon burned entirely to the dioxide, with practically no monoxide. But with as little as 0.2 percent of catalyst, the $CO:CO_2$ ratios were altered as shown:

Catalyst	Molar ratio of CO to CO_2 in combustion products
Phosphorus oxychloride	8.4
Phosphorus trichloride	6.4
Chlorine	2.9
Carbon tetrachloride	2.6
Chloroform	2.3
Stannic chloride	2.1
Dichloromethane	1.1
Hydrogen chloride	1.16
Sulfur trioxide	0.52
Iodine	0.59

Increasing the catalyst beyond 0.2 percent produced very little further change in the results. As little as 0.2 percent of water vapor in the air stream, however, largely destroyed the effect of such hydrophobic catalysts as carbon tetrachloride. The poisoning effect of water may be due to the water-gas reaction, $CO + H_2O \longrightarrow CO_2 + H_2$. Catalysts with a strong affinity for water, such as the phosphorus compounds, were better able to compete with carbon monoxide for the water molecules and thereby retain their catalytic power.

The catalysts studied by Arthur and Bowring, of course, are too volatile to be directly applicable to the glowproofing of wood, but the experiments suggest the mechanism by which more practicable glow retardants act in wood or other cellulosic materials.

Little (72) reported studies of glowing combustion independently of flaming combustion of untreated and treated cotton by first pyrolyzing the specimens in nitrogen at 350° C. and then igniting them in air with a pilot flame, noting the loss in weight during pyrolysis, loss in weight by glow, and time of glow. The results appear in table 8. Ammonium sulfamate and borax, which retard flaming well, greatly increased the extent and time of glowing, perhaps because they increased the amount of char. Boric acid, which did not prevent flaming despite the high production of char, almost completely prevented glowing. Monoammonium phosphate prevented both flaming and glowing and was highly effective against glowing at a retention as low as 0.5 percent, although a considerably higher retention was necessary for good flameproofing.

The relative performance of borax and boric acid indicates that the acid or its anhydride must be released at combustion temperatures to prevent glowing. Similarly, among the phosphates the acid is the effective agent as is shown in table 9 (72). To the extent that the acid is neutralized in sodium salts, which are stable at combustion temperatures, it is rendered ineffective against glowing.

That the effective phosphates, and presumably other glow retardants, act like the catalysts in the experiments of Arthur and Bowring to increase the CO:CO_2 ratio in the combustion products is indicated by the data of table 10 (72). Untreated cotton fabric and fabric treated with 5 percent of diammonium hydrogen phosphate was first pyrolyzed in nitrogen for varying lengths of time; it was then burned in air in a "combustion train" at 500° C. and the content of carbon dioxide and carbon monoxide determined in the emergent gases. From untreated fabric the quantities of CO and CO_2 were about the same for fabric that was partly or completely prepyrolyzed, and the ratio of CO to CO_2 was less than 0.2. From treated fabric the production of CO_2 diminished and that of CO increased with length of prepyrolysis until -- for fully prepyrolyzed fabric -- the ratio CO : CO_2 attained was nearly 1.5, or 8 to 9 times the ratio for untreated fabric. The effect of the phosphate on the CO: CO_2 ratio was less for partly than for completely prepyrolyzed fabric; presumably because water and hydrocarbons were still formed in the combustion of incompletely prepyrolyzed char to poison the phosphate catalyst. Thus glow retardants attain their full effect after pyrolysis has been completed, when glow retardance becomes most useful.
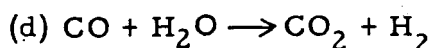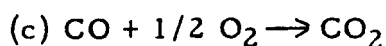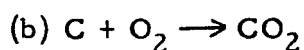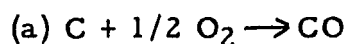
As little as 1 percent of diammonium hydrogen phosphate suffices to alter the CO:CO_2 ratio, as indicated in table 10, and heavier treatments cause little

or no further change (72). Boric acid and other effective glow retardants similarly alter the CO:CO$_2$ ratio, whereas ineffective glow retardants do not.

There is good evidence, therefore, to support the theory that glow retardance depends on catalysis of the oxidation of carbon in which the less exothermic primary reaction $(C + 1/2\, O_2 \longrightarrow CO)$ is favored at the expense of the much more exothermic secondary oxidation to carbon dioxide. On the other hand the stimulation of glow by chromates, molybdates, halides of chromium, manganese, cobalt, and copper (49) and ferric and stannic oxides (69, 104) may be attributed to catalytic promotion of the secondary oxidation of the monoxide or of a primary oxidation of carbon directly to the dioxide. It is reported that many metallic oxides lower the ignition temperature and hasten the burning of carbon (62). It is also reported that manganese dioxide catalyzes the oxidation of carbon monoxide to carbon dioxide (137). Moreover the catalytic effect of the metallic oxides in directing oxidation toward carbon dioxide can be poisoned by alkalies even in mere traces (69, 137).

There are at least three possible mechanisms for the action of catalysts in directing the oxidation of carbon and thereby the tendency to propagate glowing:

1. The catalysts may alter the energy barriers (heats of activation) of one or more of the oxidation reactions (20):

(a) $C + 1/2\, O_2 \longrightarrow CO$

(b) $C + O_2 \longrightarrow CO_2$

(c) $CO + 1/2\, O_2 \longrightarrow CO_2$

(d) $CO + H_2O \longrightarrow CO_2 + H_2$

In such alteration, the glow retardants lower the energy barrier for reaction (a) or raise the barriers for reactions (b), (c), and (d). Glow stimulators raise the barrier for reaction (a) or lower that for one or more of the other reactions.

2. The catalysts may effect regenerative cycles of such reactions as the following (attributed to W. A. Sisson by Coppick (20)):

$$2\, H_3PO_4 + 5\, C \longrightarrow 2\, P + 5\, CO + 3\, H_2O$$

$$4\, P + 5\, O_2 \longrightarrow 2\, P_2O_5$$

$$P_2O_5 + 5\, C \longrightarrow 2\, P + 5\, CO$$
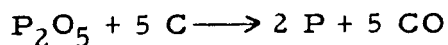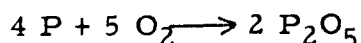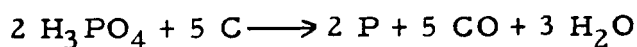
This cycle would be for a glow-inhibiting catalyst. By analogy, perhaps the following might be for a glow-stimulating catalyst:

$$2\ SnO_2 + C \longrightarrow SnO \cdot SnCO_3$$

$$SnO \cdot SnCO_3 \longrightarrow 2\ SnO + CO_2$$

$$2\ SnO + O_2 \longrightarrow 2\ SnO_2$$
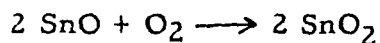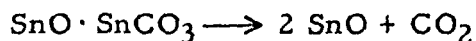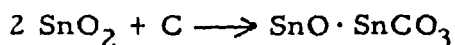
3. The catalysts may be adsorbed at active centers on the charcoal to alter its reactivity (2):
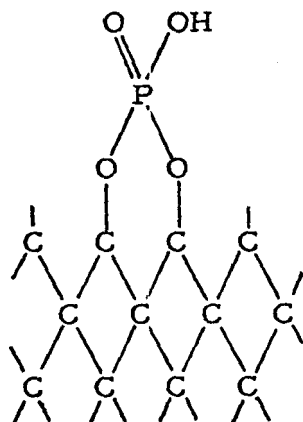
The third theory seems to provide for glow retardance but not for stimulation or for alteration of the $CO:CO_2$ ratio when oxidation does proceed. It might, however, be the initial step in the cycles of reactions of the second theory. Thus:

$$HPO_2 + 2\ CO$$

Then

$$4HPO_2 + O_2 \longrightarrow 2\ P_2O_5$$
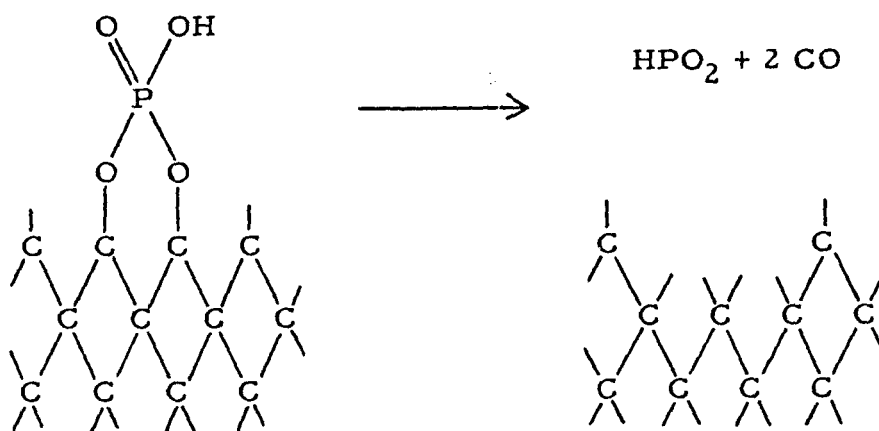
On the other hand, for the glow-stimulating stannic oxide the reaction scheme may be:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$

Then the structure reacts:

$$OSn \cdot Sn \overset{O}{\underset{O}{\diamond}} C{=}O \longrightarrow 2\,SnO + CO_2$$
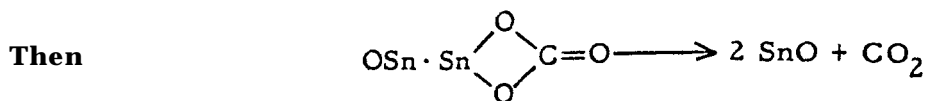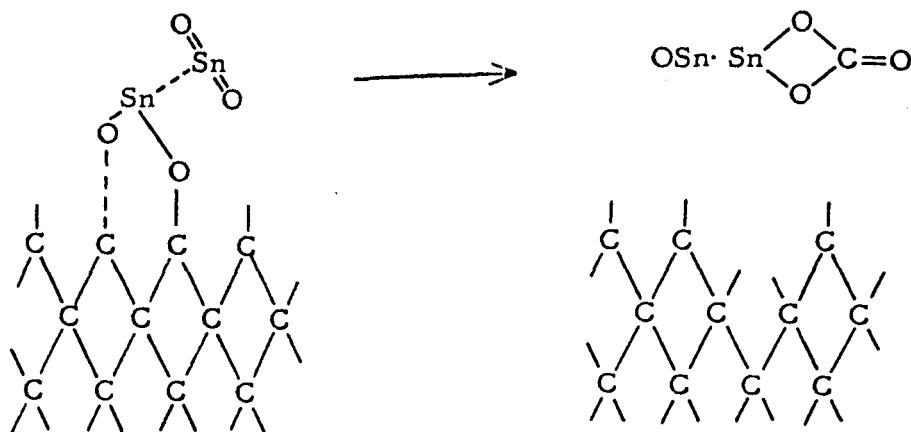
As already pointed out, the glow-inhibiting catalysts that produce a high CO:
C O$_2$ ratio with low liberation of heat may become inoperative in the presence
of water vapor. The interference may occur through the water gas reaction:

$$CO + H_2O \rightleftharpoons CO_2 + H_2$$
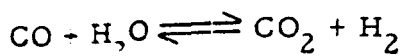
This could be followed by oxidation of the hydrogen to regenerate water, thus
setting up a branching chain reaction (72). Pyrolysis and flaming combustion
release much water, the quantity of which is further increased if flame "re-
tardants are present. During that stage of burning, glow inhibitors have little
or no effect. Those retardants like diamrnonium hydrogen phosphate, which
inhibit both flame and glow, act by entirely different mechanisms in the two
regions of burning. The mechanism of glow inibition comes into play when
charring has reached a point at which most of the water has been given off.
Successful glow inhibitors must remain with the char at this point, and must
have enough affinity for water to compete with carbon monoxide for it and then
remove the water at the beginning of the reaction chain. Since few substances
combine these two properties, good glow inhibitors are scarced.

Ammonium sulfate, ammonium, borate, and the ammonium phosphates -- in
that order-- are increasingly effective against glow. The ammonium salts de-
compose to the corresponding acids or acid anhydrides before temperatures
are reached at which wood pyrolyzes rapidly. The acids and thier anhydrides
have strong affinity for water and catalyze the dehydration of cellulose to in-
hibit flaming by mechanisms described previously. By the time complete char-
ring is attained, sulfuric acid is largely orentirely dissipated because its an-
hydride is volatile. Little (7 2), without quoting authority, says that such de-
composition of sulfuric acid into sulfur trioxide and water begins at 150° to

180° C.; others (67, 82) report temperatures as high as 340° C. In any case the loss of retardant should be serious before conditions favorable for glowing combustion of the char are reached. The anhydrides of boric acid and of phosphoric acid, however, are volatile to no more than a limited extent, even at temperatures well beyond red heat. The effective glow retardants are known to be held tenaciously by charcoal (20).

Little (72) suggests the following transitions of boric acid to its anhydride:

$$2 H_3BO_3 \text{ (at 80° to 100° C.)} \longrightarrow 2 HBO_2 + 2 H_2O$$

$$4 HBO_2 \text{ (at 167° C.)} \longrightarrow H_2B_4O_7 + H_2O$$

$$H_2B_4O_7 \text{ (at 276° C.)} \longrightarrow 2 B_2O_3 + H_2O$$
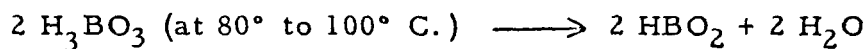
Boric oxide begins to soften at 577° C., becomes liquid at 1300° C., and boils at 1500° C. (82). Boric acid, however, is appreciably volatile with steam even at 100° C. (82). Accordingly, the slight inferiority of the berates to the phosphates as glow inhibitors may come from such loss of boric acid with the steam evolved during the charring stage of decomposition.

For phosphoric acid, Little (72) suggests the following transitions:

$$2 H_3PO_4 \text{ (at 225° C.)} \longrightarrow H_4P_2O_7 + H_2O$$

$$H_4P_2O_7 \text{ (slowly between 290° and 900° C.)} \longrightarrow 2 HPO_3 + H_2O$$
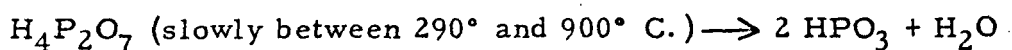
Metaphosphoric acid does not vaporize until the temperature exceeds 850° C., after which it vaporizes without decomposition. Thus metaphoric acid remains firmly with the residue after charring, where it can exercise its ability to retard glow.

Conclusion

Substantial progress has been made in reaching an understanding of the fundamental mechanisms of the pyrolysis and combustion of wood and of their alteration by added chemicals. No single theory completely describes the manner in which resistance to fire is imparted to wood. In particular, the mechanism of protection against flaming combustion differs essentially from that against glowing combustion. For resistance to both flame and glow the older physical theories no doubt remain applicable to a certain extent, at least in some cases, but the newer chemical theories seem to be of greater and more

general significance.   The chemical theories especially offer promise of achieving good resistance to fire with smaller expenditures of chemicals than have generally been found necessary in the past.

All of the theories, however, still remain too highly speculative because there has been insufficient experimental work to establish properly the extent of their validity and the quantitative details of their applicability.   But enough has been learned to afford a good foundation for a thoroughly scientific approach to the problem of imparting better fire resistance to wood.   Since empirical efforts for more than a century have added so little to our stock of practicable fire retardants for wood, it is high time that the objective be sought from the point of view of fundamental principles.

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Table 1.--Variation in yields of products in carbonization of birch at different rates and under different pressures

Time required to complete pyrolysis	Pressure	Yield of products, based on weight of moisture- and ash-free wood				
		Charcoal	Tars	Water	Carbon dioxide	Carbon monoxide
Hours		Percent	Percent	Percent	Percent	Percent
8	5mm Hg	19.54	37.18	16.64	5.95	3.28
3	atmospheric	25.51	18.0	....	....	....
8	....do.....	30.85	16.94	20.48	10.17	3.57
16	....do.....	33.18	10.1	....	....	....
336	....do.....	39.44	1.8	26.08	12.62	2.19

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Table 2.-- Activation energies and frequency factors for weight during pyrolysis of wood, wood components, and other cellulosic materials

Material	Activation energy, E (Kilocalories per mole)	Frequency factor, A (Second^{-1})	Temperature range (°C.)
Data reported by Stamm:			
Douglas-fir sawdust	25.0	1.9×10^9	110 to 220
Alpha-cellulose from Douglas-fir	26.0	4.8×10^9	110 to 220
Hemicellulose from Douglas-fir	26.7	3.6×10^{10}	110 to 220
Lignin from Douglas-fir	23.0	1.4×10^{10}	110 to 220
Coniferous wood (southern and white pine, Sitka spruce, Douglas-fir)	29.5	5.1×10^{11}	94 to 250
Sitka spruce	29.8	2.3×10^{11}	167 to 300
Data of Kujirai and Akahira:			
Manila paper	31.7	2.8×10^{12}	145 to 265
Linen	31.0	4.5×10^{11}	165 to 265
Filter paper	31.0	7.5×10^{11}	165 to 265
Cotton	32.1	1.3×10^{12}	165 to 265
Data of Madorsky, Hart, and Straus:			
Cotton	50		275 to 305
Hydrocellulose (cotton treated with 6N HCl)	47		285 to 305
Viscose rayon	49		265 to 295
Cellulose triacetate	45		297 to 320
Cellulose regenerated from cellulose triacetate	46		285 to 300
Cotton impregnated with 8 percent of sodium chloride	35		255 to 285
Cotton impregnated with 9 percent of sodium carbonate	19		255 to 285
Viscose rayon impregnated with 9 percent of sodium carbonate	30		245 to 275

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Table 3. --Relation between foaming tendency and flame retardance for cotton fabric

Foaming tendency[1]	Flame retardant	Flame retardance		
		Reten- tion	Char area	After- flame
Inch		Percent	Sq. in.	Seconds
4.50	Boric acid, ammonium dihydrogen phosphate (1:1)	51.0	1.44	0
3.50	Borax, boric acid (1:1)	7.7	1.67	0
3.50	Sodium phosphate, boric acid (1:1)	10.5	2.06	0
3.25	Borax, boric acid, diammonium phosphate (7:3:5)	9.5	1.90	0
3.25	Borax, boric acid (7:3)	9.5	2.19	0
2.75	Commercial borate mixture	8.4	2.08	0
2.75	Borax, boric acid, diammonium phosphate (1:1:2)	8.8	2.86	0
2.50	Borax, diammonium phosphate (1:1)	7.9	2.84	0
2.75	Borax	15.8	burned to end	39
2.00	Aluminum sulfate	8.8	4.59	0
.25	Boric acid	9.3	burned completely	70

[1] Height of foam from 5 grams of retardant in a 1-inch test tube when heated at 450° to 500° C.

Table 4.--Lowering of the charring temperature of cotton fabric by fire-retardant chemicals

Fire retardant	Amount of retardant in fabric	Charring temperature
	Percent by weight	°C.
None (untreated fabric)	0	340
Ammonium bromide	7	200
Ammonium chloride	38	220
Ammonium phosphate	12	250
Ammonium sulfate	8	240
Borax	60	310
Boric acid	90	320
Borax: Boric acid (7:3)	15	315
Calcium chloride	14	280
Sodium silicate	20	310
Sodium tungstate	9	305
Zinc chloride	12	230

Table 5.--Yield of charcoal in combustion of treated and untreated cotton fabric

Added chemical	Charcoal residue from fabric containing the indicated percentage by weight of chemical								
	0	2	8	10	11	12	15	20	28
	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent	Percent
Ammonium bromide	19	30	44	45		45.5		48	
Ammonium phosphate	19		39						
Borax	19				40				
Borax: Boric acid (7:3)	19	38	43.5	44		44.5		46	
Sodium dihydrogen phosphate[1]	19								28
Disodium hydrogen phosphate[1]	19								
Trisodium phosphate[1]	19						29		
Sodium tungstate	19					36	27		
Sodium vanadate	19	27	29	29.5		30		31.5	
Sodium chloride[1]	19	17	14	14		14		14	

[1] Sodium chloride is not a fire retardant and the sodium phosphates are very poor fire retardants.

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Table 6.—Yields of tar, aqueous condensate, and gases in combustion of treated and untreated cotton fabric

	Quantity of chemical added	Dry tar	Aqueous condensate	Total dry gas	Components of gas by volume				Vertical after flaming [1]
					Acids, etc.	CO	Hydrocarbons	CO_2	
	Percent	Mg. per cm.² of fabric		Cc. per cm.²	Percent	Percent	Percent	Percent	Seconds
Sodium chloride [2]	0	12.20	9.24	1.04	43.2	32.5	14.2	10.1	23
	3.1	7.05	14.31	3.67	35.8	30.8	18.6	14.8	20
	7.0	7.80	10.25	3.77	36.2	31.8	18.5	13.5	25
	13.5	6.50	13.88	1.96	35.3	32.5	18.1	14.1	23
	26.4	6.43	14.37	3.22	35.9	32.3	20.5	11.3	23
	33.7	7.48	14.02	2.45	38.7	25.0	21.4	14.9	28
Boric acid [2]	0	12.20	9.24	1.04	43.2	32.5	14.2	10.1	23
	3.5	7.86	15.90	1.50	34.6	41.0	14.5	9.9	28
	7.7	6.53	15.65	1.75	30.8	44.3	15.2	9.7	26
	10.5	4.52	15.03	1.81	31.4	46.0	13.0	9.6	28
	12.9	4.00	14.15	1.92	27.1	48.3	15.8	8.8	28
Borax	0	12.20	9.24	1.04	43.2	32.5	14.2	10.1	23
	2.8	4.55	4.76	2.41	29.0	36.4	15.6	19.0	15
	5.4	2.62	14.25	2.17	34.6	33.7	16.3	15.4	3
	12.9	3.08	15.90	2.25	34.6	36.2	13.1	16.1	3
	20.3	2.88	15.28	2.10	36.2	37.0	12.4	14.4	3
	29.0	2.08	14.65	2.15	40.0	27.0	18.0	15.0	3
	34.5	2.75	15.86	2.29	34.9	29.8	19.5	15.8	0
Borax : Boric acid (7:3)	0	12.20	9.24	1.04	43.2	32.5	14.2	10.1	23
	2.6	3.18	12.57	2.03	39.5	33.5	16.9	10.1	18
	4.6	1.97	13.26	2.50	37.9	33.9	18.0	10.2	0
	8.4	1.28	13.90	2.30	38.6	37.9	12.7	10.8	0
	16.4	0.85	12.48	2.45	39.2	33.8	16.4	10.6	0
	30.1	.83	14.49	2.54	36.9	36.4	13.9	12.8	0
	43.7	.55	10.10	2.35	42.3	33.5	12.1	12.1	0

[1] With effective fire-retardant treatment there is little or no afterflaming.

[2] Sodium chloride and boric acid are not flame retardants.

Table 7. --Yields of char, tar, water, and carbon dioxide in the combustion of treated and untreated cotton fabric

Retardant	Temperature	Char	Tar	Water	Carbon dioxide
	°C.	Percent	Percent	Percent	Percent
Diammonium phosphate (14 percent)	550	36	22	39	5
	350	45	7	47	4
Borax-boric acid (13 percent)	500	41	5	40	9
	350	57	1	33	8
Erifon (complex of titanium oxide and antimony oxide)(10 percent)	500	37	12	35	6
	350	49	5	37	7
None (untreated fabric)	500	8	54	29	6
	350	12	42	33	6

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Table 8. --Retardation of glowing combustion of the char from fabric that was first pyrolyzed in nitrogen

Retardant	Amount of retardant retained in fabric	Loss in weight		Time of glowing
		During pyrolysis	By glowing	
	Percent	Percent	Percent	Seconds
None (control) [1]	0	79.5	18.8	73
Sodium chloride [1]	10	67.0	8.6	62
Ammonium sulfamate [2]	10	54.0	37.7	360
Borax [2]	10	60.0	27.4	180
Boric acid [3]	10	54.5	1.5	0
Ammonium dihydrogen phosphate [4]	10	55.2	0.2	0
Ammonium dihydrogen phosphate	0.5	68.9	3.1	9

[1] Poor retardant of either flame or glow.

[2] Good retardant of flame but not of glow.

[3] Poor retardant of flame but good retardant of glow.

[4] Good retardant of both flame and glow.

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Table 9.--Relative glow retardance of phosphates

Retardant	Amount of retardant retained in fabric	Time of glowing	Char area (for test method see reference 71)
	Percent	Seconds	Square inches
$Na_3PO_4 \cdot 12H_2O$	77.5	400	Completely consumed
$Na_2HPO_4 \cdot 12H_2O$	57.4	70	Completely consumed
$NaH_2PO_4 \cdot H_2O$	16.9	0	2.4
H_3PO_4	14.8	0	2.5

Table 10. --Effect of diammonium hydrogen phosphate on the gases produced by combustion of char from cotton fabric that had been previously pyrlyzed for varying lengths of time

Time of initial pyrolysis	Carbon dioxide from			Carbon monoxide from			Molar ratio, CO per CO_2		
		Untreated fabric	Treated fabric		Untreated fabric	Treated fabric		Untreated fabric	Treated fabric
Minutes		Grams	Grams		Grams	Grams			
10		2.29	2.09		0.252	0.472		0.173	0.355
15		2.42	1.70		.256	.585		.166	.540
20		2.60	1.55		.210	.833		.127	.840
30		2.42	1.16		.294	1.10		.191	1.49