HEAT RELEASE IN THERMALLY DISINTEGRATING WOOD[1]

Hans Kubler

Associate Professor

Department of Forestry, University of Wisconsin, Madison, WI 53706

ABSTRACT

Wood contains more energy than do its products of slow pyrolysis. Consequently, slow pyrolysis must be an exothermic process, and cannot consume heat as generally believed. Heat release in experiments with thermally slowly decomposing wood has indeed been reported in the literature. The exothermic nature of pyrolysis explains why wood self-heats when its temperature has been somehow raised above 80 C and when the released heat does not dissipate. This way the temperature may reach the level of oxidation and combustion. Such pyrolytic self-heating occurs in piles of sawdust, wood chips, and bark, in hot-stacked boards and paper rolls, in dryers for veneer and other wood, and in structural lumber near heat sources. In contrast to other kinds of self-heating, pyrolytic self-heating cannot be prevented by exclusion of oxygen; instead the process has to be decelerated by cooling the material.

Keywords: Pyrolysis, thermal decomposition, exothermic point, self-heating, spontaneous ignition, heat of combustion.

INTRODUCTION

In piles of wood chips, sawdust, bark, chopped whole-tree material, and bales of waste paper, temperatures may rise without any influx of heat (Riley 1979). Other wood products self-heat after their temperature has been raised by an external source, among them kiln-dried fiber insulating boards piled while still above 90 C (Holmgren 1948), hardboard during the tempering process (Ostlin 1959), veneer and pieces for wood-base panels in dryers, structural lumber close to hot items such as steam pipes (Matson et al. 1959), and paper rolls stacked in the mill while still hot.

The various self-heating processes as such involve loss of mass and chemical changes that impair the recovery of pulp and paper from wood (Bergman 1974). The generated heat causes wood decomposition along with discoloration, in this way affecting wood strength to the point of charring (Schaffer 1966) and reducing the fuel value (Browne and Brenden 1964). The damage increases progressively as the temperature rises, at times leading to smoldering combustion (Schaffer 1979) or culminating in spontaneous ignition and fire hazards in dryers, in buildings, in vehicles during transport of forest products, and in wood piles outdoors.

OPINIONS ABOUT CAUSES OF SELF-HEATING

Springer et al. (1971) showed convincingly that living parenchyma cells in fresh wood chips generate heat as they respire. Between 50 and 60 C, the cells die and cease respiring, but then the metabolism of microorganisms releases heat (Mess-

ner and Serentschy 1978), until at near 80 C even the most heat-resistant (thermophilic) microbes perish (Jach 1973).

It is generally believed that above 80 C direct chemical oxidation is responsible for further self-heating (Tsuchiya and Sumi 1977). However, in piles of wood chips, sawdust, bark, and particularly stacks of hot fiberboard, self-heating is much greater in the center than near the surface, indicating that some process other than oxidation—possibly thermal disintegration—generates heat. True, surfaces of the pile remain cooler mainly because heat dissipates into the environment, but the temperature differences within the piles cannot be explained by dissipation of heat alone.

According to the literature (Browne 1958; Aaron 1980), until the level of 280 C, thermal disintegration or decomposition (pyrolysis) of wood absorbs heat and is endothermic. Only at higher temperatures is the process believed to be exothermic, and may cause self-heating. This view of an exothermic point near 280 C is apparently based on thorough studies by Klason et al. (1909 and 1910), who heated 800-g batches of cellulose and wood in a retort at normal pressure at 400 C within 8 h. The temperature in the sample's center lagged behind the surface temperature, except around 270 to 330 C, where it rose higher. The exothermic point 280 C seems to agree with practical field experience in charcoal production, where in retorts, kilns, pits, or piles some of the wood is burned to raise the temperature to a point at which it continues to rise in the absence of air, without combustion. Klason et al. (1909) reasoned, however, that pyrolysis gives off heat up to 400 C; later (1910) they concluded that the amount of heat given off is greater when pyrolysis proceeds at lower temperatures. In their experiments, heat release or exothermicity was undetectable as long as the retort was much hotter than the sample and, therefore, imposed a temperature gradient on the sample. Only when at around 270 C the sample temperature approached that of the retort, and when the heat release became significant, the center became hotter than the surface. At that point the exothermic nature of pyrolysis became obvious, but the material probably had given off heat long before.

It is the objective of this study to clarify the thermal balance of wood pyrolysis, to find out under which conditions pyrolysis becomes exothermic, and particularly to discover whether slow pyrolysis releases heat.

APPROACH

The thermal balance or heat of pyrolysis (ΔH) is calculated by means of this corollary of the first law of thermodynamics:

$$\Delta H = \Sigma \Delta H^c_r - \Sigma \Delta H^c_p \qquad (1)$$

The symbol ΔH^c means heat of combustion, while the indices stand for pyrolysis reactants (r) and pyrolysis products (p).

As an example, let us calculate the alcoholic fermentation of the sugar glucose, a reaction which is related to pyrolysis of wood constituents:

glucose → ethyl alcohol + carbon dioxide

$$C_6H_{12}O_6 \rightarrow \quad 2C_2H_5OH \quad + \quad 2CO_2$$
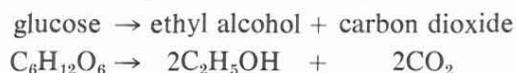
Heats of combustion are −2,810 kJ/mole for the reactant glucose, −1,411 kJ/mole for the product ethyl alcohol, and of course zero for carbon dioxide (Table 1;

TABLE 1. *Heats of combustion*[a] *and related data for wood pyrolysis compounds.*

Compound	State	Formula	Weight	Heat of combustion	
				kJ/mole	kJ/g
Hydrogen	gas	H_2	2.016	−286.0	−141.88
Water	liquid	H_2O	18.015	0	0
Water	gas	H_2O	18.015	−44.0	−2.44
Carbon (graphite)	solid	C	12.011	−393.8	−32.78
Carbon monoxide	gas	CO	28.011	−283.2	−10.11
Carbon dioxide	gas	CO_2	44.010	0	0
Methyl alcohol	gas	CH_3OH	32.042	−764.6	−23.86
Formaldehyde	gas	HCHO	30.027	−563.8	−18.78
Formic acid	liquid	HCOOH	46.026	−254.8	−5.54
Formic acid	gas	HCOOH	46.026	−301.0	−6.54
Ethyl alcohol	gas	C_2H_5OH	46.070	−1,411.0	−30.63
Acetaldehyde	gas	CH_3CHO	44.054	−1,193.4	−27.09
Acetic acid	liquid	CH_3COOH	60.053	−875.0	−14.57
Acetic acid	gas	CH_3COOH	60.053	−925.1	−15.41
Ketene	gas	CH_2CO	42.038	−1,012.4	−24.08
Glyoxal	gas	$C_2H_2O_2$	58.037	−759.4[b]	−13.08
Acetone	gas	$(CH_3)_2CO$	58.081	−1,822.6	−31.38
Furane	gas	C_4H_4O	68.076	−2,112.5	−31.03
Furfural	liquid	C_4H_3OCHO	96.086	−2,342.5[c]	−24.38
Levoglucosan	solid	$C_6H_{10}O_5$	162.144	−2,837.4[b]	−17.50
Charcoal	solid	$C_{16}H_{10}O_2$	234.255	−7,507.9[d]	−32.05
Methane	gas	CH_4	16.043	−891.0	−55.54
Acetylene	gas	C_2H_2	26.038	−1,300.5	−49.95
Ethylene	gas	C_2H_4	28.054	−1,411.9	−50.33
Ethane	gas	C_2H_6	30.070	−1,560.9	−51.91
Xylose	solid	$C_5H_{10}O_5$	150.133	−2,340.4[e]	−15.59
β-D-Glucose	cryst.	$C_6H_{12}O_6$	180.159	−2,809.9	−15.60
Cellulose	solid	$(C_6H_{10}O_5)_n$	162.144	−2,838.2[b]	−17.50
Lignin	solid	$C_{40}H_{44}O_6$	620.788	−16,314.7[f]	−26.28
Wood	solid	$C_{42}H_{60}O_{28}$	1,012.930	−20,262.6[g]	−20.00

[a] Some values are calculated from published heats of formation, which generally are based on measured heats of combustion. Unless another source is given, the numbers originate from Gray, D. E. (ed.) et al. 1972. American Institute of Physics handbook, 3rd ed. McGraw Hill, New York. Ch. 4.

[b] Kharash, M. S. 1929. Heats of combustion of organic compounds. Bur. Standards J. Res. 2:384–389.

[c] Dean, J. A. 1973. Handbook of chemistry, 11th ed. McGraw Hill, New York. Pages 9–96.

[d] Klason et al. (1910), see references.

[e] Weast, R. C. 1972. Handbook of chemistry and physics, 53rd ed. Chem. Rubber Co., Cleveland, OH. Page D279.

[f] Brauns, F. E. 1952. The chemistry of lignin. Page 442 *in* L. E. Wise and E. C. Jahn. Wood chemistry, 2nd ed., vol. 1. Reinhold Publ. Corp., New York.

[g] Hawley, L. F. 1952. Combustion of wood. Page 822 *in* L. E. Wise and E. C. Jahn. Wood chemistry, 2nd ed., vol. 2. Reinhold Publ. Corp., New York.

following physical chemistry customs, heat of combustion is expressed in negative numbers, as being the heat given off by the system). With these values in Eq. (1), we obtain

$$\Delta H = -2,810 - [2 \times (-1,411) - 0] = +12 \text{ kJ/mole}$$

meaning the reaction consumes +12 kJ per mole of glucose.

Calculating heat of wood pyrolysis with Eq. (1) appears to be impossible because wood pyrolysis involves many complex reactions that depend heavily on numerous variables and are in part unknown. The reactions, however, do not

have to be known in detail along with all intermediate products; it suffices to know the entering reactants and final products. The overall heat of a chemical reaction remains the same regardless of the intermediate stages involved.

Heats of combustion have been measured accurately for numerous compounds by the U.S. National Bureau of Standards and by others. The heats of interest in this study are listed in Table 1, in units of kJ/mole and kJ/g. When calculating the thermal balance, the mole as reaction quantity is advantageous, whereas for comparisons of identical masses, gram units are preferable. All heats of combustion apply to the standard state, that is, normal pressure and 25 C, to avoid errors due to heat capacities of the substance. The compounds are assumed to burn to liquid water and carbon dioxide gas. For cellulose, the data apply to one single link of the molecule chain rather than to the molecule as a whole.

Compounds which boil above 160 C are listed in their physical state at 25 C (solid or liquid), whereas in cases where the boiling point is below 100 C, I chose the gas state, the reason being that low-boiling products evaporate and escape from decomposing hot wood. "Dual-state" compounds between these two groups—water (boiling point 100 C), formic acid (110.5 C), and acetic acid (118.1 C)—are considered in both the liquid and the gaseous state. Near the wood surface, these compounds tend to evaporate and to escape, while deep in large wood piles a large proportion of them remain liquid or adsorbed. The energy consumed for evaporation, known as latent heat, does not appear in the thermal balance.

PYROLYSIS PRODUCTS

For the calculation we need to know which products evolve from thermally disintegrating wood, particularly from wood which decomposes slowly above 80 C. Browne (1958) compiled the major kinds of pyrolysis products in an extensive literature review about pyrolysis reactions. In rapidly heated wood, pyrolysis begins above 100 C and accelerates until the temperature approaches 300 C. Beyond this peak the reaction rate decreases even when temperature continues to rise as fast as before. Up to 200 C, oven-dry wood dehydrates, losing water of constitution which escapes as vapor mixed with traces of carbon dioxide, acetic and formic acids, and glyoxal. Between 200 and 280 C, the proportion of water vapor becomes smaller as the other volatiles appear in increasing quantities, together with carbon monoxide. Between 280 and 500 C, carbon monoxide, methane, formaldehyde, formic and acetic acids, methanol, and later hydrogen are the most notable products, still diluted with carbon dioxide and water vapor but also mixed with tars. What remains is the solid residue charcoal, generally the major product of pyrolysis in terms of mass.

Klason (1914) found that the heating rate has a strong influence on pyrolysis. When he carbonized birch in vacuum within 5 h, the percentages of produced char, water, and carbon dioxide were 19.5, 16.6, and 6, respectively. They were 39.4, 26.1, and 12.6 when heating a larger sample at normal pressure in the course of 14 days to the same temperature of 400 C. In an 8-h 400 C test, at normal pressure, the quantities were in between those of the two extreme tests—30.9, 20.5, and 10.2%. The wood tested contained 11% moisture, but this hygroscopic water is disregarded in the given percentages.

In tests with sawdust, which lasted only from 2 to 390 min and ended either at

TABLE 2. *Products evolving in models for slow and fast pyrolysis of 10 moles of oven-dry wood.*

Product	Number of moles for pyrolysis rate		Weight (percent) for pyrolysis rate	
	Slow	Fast	Slow	Fast
Hydrogen	—	80	—	1.59
Water	119	5	21.16	0.89
Carbon monoxide	6	52	1.66	14.38
Carbon dioxide	17	26	7.39	11.30
Methyl alcohol	13	15	4.11	4.74
Formic acid	4	36	1.82	16.36
Acetic acid	21	23	12.45	13.64
Glyoxal	9	—	5.16	—
Furfural	—	15	—	14.23
Acetylene	—	53	—	13.62
Charcoal	20	4	46.25	9.25

525 or at 600 C, more rapid carbonization yielded less acid, less alcohols, and again less charcoal (Goos et al. 1948). Among volatiles of slowly decomposing cellulose in vacuum at 160 C, the $H_2O/CO_2/CO$ ratios were 2/0.75/1 at the end of the drying phase, but one month later when the decomposition was much slower they were 10/2.5/1 (Murphy 1962). In experiments reported by Demidov (1962), the proportion of carbon monoxide among the volatiles increased as wood temperature rose, peaking around 400 C; hydrogen and the hydrocarbons methane, acetylene, and ethane appeared only at temperatures of 300 C and higher.

In slow pyrolysis, "the decomposition proceeds in an orderly manner in which there is stepwise formation of increasingly stable molecules" whereas "in very rapid heating, macromolecules may be literally torn into volatile fragments with little possibility of orderly arrangement" (Browne 1958, p. 7).

Moisture accelerates wood decomposition through hydrolysis, that is, a chemical process in which a compound reacts with the ions of water. Hydrolysis splits hemicellulose and cellulose—wood's main constituents, besides lignin—into sugars, acetic acid, and formic acid. These are products that are known to evolve when wood is steamed or "boiled" at 70 to 100 C to soften it for veneer cutting and for other purposes (Plath and Plath 1955). The acids catalyze and accelerate further hydrolysis, particularly when trapped in the wood.

Strictly speaking, hydrolysis is not a kind of pyrolysis, since acids and alkalis catalyze wood already at room temperature. Hydrolysis without added chemicals, however, requires temperatures that are nearly as high as those of pyrolysis. Besides, pyrolysis is generally accompanied by hydrolysis even in oven-dry wood, where the evolving water of constitution acts as an hydrolytic agent. For these reasons, hydrolysis is here treated as a kind of pyrolysis.

HEAT OF PYROLYSIS CALCULATION FOR WOOD AS A WHOLE

Here the thermal balance is calculated for slow and for fast pyrolysis. Unfortunately, complete quantitative analysis data are not available and are difficult to determine. Pyrolysis researchers have either identified only the kind of evolving products, or have measured the quantity of only some products. Klason (1914) analyzed the process rather completely, but for some of his tars, oils, and other

TABLE 3. *Thermal balance in models of slow and fast pyrolysis when "dual-state" products evolve either as liquid or as gas.*

Unit of measurement	State	Pyrolysis rate	
		Slow	Fast
kJ/mole	liquid	−1,460	984
	gas	−813	1,288
Percent of wood's heat of combustion	liquid	7.2	−4.9
	gas	4.0	−6.4

products, reliable heats of combustion are not available. I therefore use reaction models in which the products consist of wood's atoms ($C_{42}H_{60}O_{28}$). Other constraints are flexible: the model for slow pyrolysis should feature mainly products that evolve in slow pyrolysis, while in the fast-pyrolysis model typical fast-pyrolysis products are preferred (Table 2). Though the models are to some extent arbitrary, they serve their purpose: to show how rates of pyrolysis affect the thermal balance.

Accordingly, slow pyrolysis releases plenty of heat, whereas fast pyrolysis is endothermic (Table 3). The −813 kJ/mole evolving in slow pyrolysis (in the case of gaseous dual-state products) amount to 4% of the heat of combustion of oven-dry wood, and are in good agreement with calculations by Klason (1914), explained below. The −813 kJ/mole exceed the specific heat of oven-dry wood at 100 C (1.6 kJ/mole C) by a factor of 500. Theoretically, released heat can raise wood temperature by hundreds of degrees.

In the models it is assumed that the dual-state products either evaporate or do not. In reality, some evaporate and some remain liquid or are adsorbed, but in fast pyrolysis a higher proportion evaporates than in slow pyrolysis because temperatures and vapor pressures are higher. The longer time available for evaporation and migration out of slowly decomposing wood cannot compensate for the higher vapor pressure gradient in fast pyrolysis. These facts strengthen the influence of the pyrolysis rate on the thermal balance.

Klason's (1914) 14-day trial cannot serve as a good example of slow pyrolysis because he heated the wood first rapidly, before raising the temperature step by step within two weeks to 400 C. In his trial in vacuum, in which the temperature rose to 400 C within 5 h, he obtained 41% of tars and oils which at higher temperatures would decompose into better defined products. Nevertheless the thermal balances for these trials are interesting. I calculated them on the basis of heats of combustion from Table 1, except that I used Klason's heats of combustion for birch, charcoal, tars, and oils, which he determined himself for each trial, without explaining how. Assuming the dual-state products evolved as gas, the heat of pyrolysis was in the 14-day trial 3.4%, in the 8-h trial 2.5%, and in the 5-h trial 0.1% of oven-dry wood's heat of combustion. Assuming liquid dual-state products, the percentages were 6.9, 5.2, and 2.4, respectively. Klason calculated almost identical values (7.1, 5.3, and 2.6, respectively), even though precise heats of combustion were not available in his time; inaccuracies apparently cancelled out.

Trees synthesize wood from carbon dioxide and water under direct and indirect consumption of solar energy. Wood decompostion into these compounds would

be a reversal of wood growth. However, for decomposition into water and carbon dioxide alone, wood lacks the oxygen that tree leaves have given off in the photosynthesis process. Nevertheless, it is of interest how much heat evolves when wood decomposes into the highest possible amounts of water and carbon dioxide. The reaction for water

$$C_{42}H_{60}O_{28} \rightarrow 28\ H_2O + CH_4 + 41\ C$$

gives off $-3,226$ kJ/mole or 15.9% of wood's heat of combustion, in case the water remains adsorbed or as a liquid in the system. If the water escapes as vapor, the thermal balance is still $-1,994$ kJ/mole or 9.8% of the heat of combustion. Decomposition into the main product carbon dioxide

$$C_{42}H_{60}O_{28} \rightarrow 14\ CO_2 + 15\ CH_4 + 13\ C$$

gives off $-1,180$ kJ/mole or 5.8% of the heat of combustion. It is assumed that pure carbon finally remains when wood is exposed to heat around 100 C for many years, although this test has not been made; but we do know that in decomposing wood the proportion of carbon increases with time (Klason 1914). To summarize, the models of reversed tree growth indicate that the maximum of pyrolytic heat lies somewhere between 6 and 16% of wood's heat of combustion.

HEAT OF PYROLYSIS CALCULATION FOR WOOD CONSTITUENTS

Heats of reaction for decomposition of cellulose as well as of cellulose and hemicellulose pyrolysis products are compiled in Table 4. Heat generated by hydrolysis depends on the state of the water reacting with the wood constituent. If in case of cellulose hydrolysis (reaction No. 1) water enters as liquid, -157.1 J evolve per gram of total weight of cellulose and water, which amounts to nearly 0.8% of the heat of combustion of 1 g of wood. In case water enters the system as vapor, the latent heat of vapor increases the heat of hydrolysis to 3% of wood's heat of combustion.

Decomposition of the hydrolysis product glucose into an abundance of the energy-free compounds water and carbon dioxide (reaction model No. 2) generates heat even when the produced water escapes as vapor. Reaction No. 3 is the total of No. 1 and 2. In models No. 2 and 3, acetone and carbon are included to accommodate elements remaining after formation of water and carbon dioxide. Acetone indeed evolves in wood pyrolysis (Klason et al. 1910), while carbon appears as the main element of charcoal. Other compounds in place of acetone and carbon (composed of the available elements) make little difference in the thermal balance, as shown in the alternative model for cellulose pyrolysis (No. 4), where the high-energy product hydrogen seems out of place since it evolves at a very high temperature; but even so the reaction releases considerable heat.

Reactions No. 5, 6, and 7 are thermal degradations of xylose, one of the sugars produced by hydrolysis of hemicellulose. Hemicellulose hydrolyzes more readily than cellulose does. Hydrolysis of hemicellulose could not be included in the table because heat of combustion is not known for the various kinds of hemicellulose. However, hemicellulose hydrolysis resembles that of cellulose and can be assumed to generate similar amounts of heat. Reaction No. 5 features acetic acid as the main decomposition product of xylose and gives off heat if the acid remains as liquid in the system. In the heat-consuming reaction No. 6, water does not

TABLE 4. *Thermal balance of pyrolysis reactions for liquid and gaseous "dual-state" compounds.*

No.	Reaction	Liquid state		Gaseous state	
		kJ/mole	J/g	kJ/mole	J/g
1	$(C_6H_{10}O_5)_n + H_2O \rightarrow C_6H_{12}O_6$	−28.3	−157.1	−72.3	−401.3
2	$C_6H_{12}O_6 \rightarrow 3H_2O + CO_2 + (CH_3)_2CO + 2C$	−199.7	−1,108.5	−67.7	−375.8
3	$(C_6H_{10}O_5)_n + H_2O \rightarrow 3H_2O + CO_2 +$				
	$(CH_3)_2CO + 2C$	−228.0	−1,265.5	−140.0	−777.1
4	$(C_6H_{10}O_5)_n \rightarrow 3H_2O + CO_2 + 5C + 2H_2$	−297.2	−1,832.9	−165.2	−1,018.8
5	$C_5H_{10}O_5 \rightarrow 2CH_3COOH + CO + H_2$	−21.2	−141.2	+79.0	+526.2
6	$C_5H_{10}O_5 \rightarrow C_4H_3OCHO + H_2O$	+2.1	+14.0	+134.1	+893.2
7	$C_4H_3OCHO \rightarrow C_4H_4O + CO$	+53.2	+553.7	+53.2	+553.7

compensate for the high heat of combustion of the main product furfural, especially not when the water escapes as vapor. Reaction No. 7 concerns liquid furfural, whose boiling point is 162 C, but even decomposition of furfural *gas* into furane and carbon dioxide would consume heat, though only 10.5 kJ/mole.

Reaction No. 6 and especially No. 7 occur in rapid pyrolysis (Browne 1958, p. 10). Slow pyrolysis of hemicellulose leads to products similar to those in the slow pyrolysis of cellulose, and gives off heat, at least when hydrolysis is taken into account. Likewise, rapid pyrolysis of cellulose resembles reactions No. 6 and 7, and is endothermic according to calculations.

Some wood pyrolysis reactions resemble the example cited of alcoholic fermentation. The fermentation reactant glucose has been mentioned as a product of cellulose hydrolysis, while the fermentation products carbon dioxide and ethyl alcohol are known to evolve from thermally disintegrating wood. In cases when the alcohol remains as usual in solution, the reaction is exothermic. This result supports the thesis that pyrolysis releases heat whenever large proportions of energy-free compounds evolve.

Lignin is a very complex and major constituent of wood which decomposes in numerous ways into a great variety of products. None of the decomposition reactions stands out among the others. Therefore Table 4 does not include decomposition of lignin, but the compound is considered in the following chapter.

ENERGY SCALE

In Fig. 1, heats of combustion are arranged in order, high-energy compounds being listed near the top. Pyrolysis that leads to products that rank below wood in this "energy scale" must give off heat, whereas pyrolysis into products above wood in the scale must consume heat (Eq. 1). Of course, this rule is of limited use when some products rank below and others above wood, as they have to because the percentage of oxygen in the products below wood is higher than that in wood, and the percentage of oxygen in the products above wood is lower than that in wood. (Any pyrolysis model in which the products consist of wood's elements must include "above wood" *and* "below wood" compounds.) Products of slow pyrolysis appear below wood with the exception of charcoal, which evolves in large amounts whenever pyrolysis proceeds at a slow rate. The energy scale obviously serves as an approximate but not an accurate indicator of the thermic nature of any kind of wood pyrolysis.
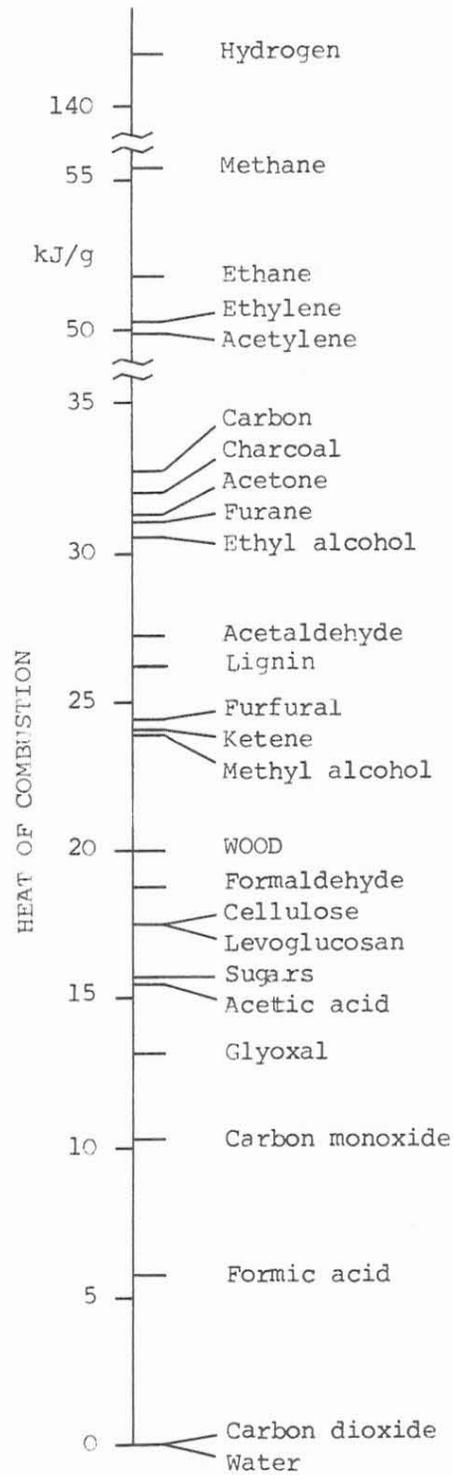
Fig. 1. Energy scale for wood pyrolysis reactants and products.

Lignin contains percentagewise more carbon and less oxygen than do cellulose and hemicellulose, consequently also more than does wood. Therefore lignin's heat of combustion is, with more than 26 kJ/g (Table 1), much higher than that of wood. But lignin also disintegrates into more charcoal and hydrocarbons (Browne 1958), products which rank high in the energy scale. For these reasons, lignin can be assumed to resemble other wood constituents, and wood itself, in heat of pyrolysis.

It has been mentioned before that when cellulose decomposes at constant temperature, the proportion of the energy-free compound carbon dioxide among the volatiles increases as time passes (Murphy 1962), that is, as the rate of pyrolysis decreases. This suggests that slow pyrolysis releases heat not only when slow due to low temperature, but also when slow due to long exposure to heat.

The rule "slower pyrolysis releases more heat" does not apply beyond the peak temperature of pyrolysis. As mentioned before, in wood whose temperature is raised rapidly, the rate of pyrolysis reaches a peak around 300 C, and above 350 C the process becomes very slow. Products that evolve near 400 C, for example, include significant amounts of hydrocarbons and other high-energy compounds, which make the pyrolysis endothermic even though the pyrolysis rate is slow. The farther the temperature rises, the higher the percentage of evolving high-energy products becomes, and the more heat the disintegration consumes. Wood that is heated very slowly decomposes long before the temperature reaches 300 C, indicating that the peak temperature of pyrolysis depends on the heating rate and is relatively low for slow heating rates. Hence the temperature up to which it is true that "slower pyrolysis releases more heat" is relatively low for slow heating rates.

We deal here with the amount of heat given off, rather than with the rate of heat release. Though pyrolysis at 100 C liberates more heat (expressed in Joules per gram) than pyrolysis at 200 C, for example, the heat release *rate* (expressed in Joules per hour and gram) is probably higher in the much shorter 200 C pyrolysis. Very likely, in slowly heated wood, the heat release rate peaks at a certain temperature at which the product of pyrolysis rate (expressed in gram per hour) and heat release (J/g) is at an optimum; this may be around 200 C.

EXPERIMENTAL EVIDENCE AND CONCLUSIONS

In view of the evidence for slow wood pyrolysis being exothermic, the question arises why pyrolytic heat release has not been noticed in experiments at lower temperatures. Actually such heat release *has* been observed in several investigations in which material was exposed to elevated temperatures within an inert atmosphere or in closed containers. Walker and Harrison (1977) noticed it on 5-liter samples of moist *Pinus radiata* sawdust at 76 to 96 C, Rothbaum (1963) in 2-liter wads of moist hay (a cellulosic material like wood) at 90 C, Widell (1948) in dry 45-mm-diameter aspen cylinders at 175 C, Kollmann (1960) in oven-dry 70-mm-diameter cylinders of beech at around 225 C and of spruce at 250 C, and Heinrich and Kaesche-Kirscher (1962) in an oven-dry 60-mm beech cube at 228 C.

The mentioned degrees are either the lowest temperatures at which heat release was noticed, or they are ranges of observed heat release. The low temperatures vary so much because they are not necessarily the points where heat release

commenced, but rather temperatures at which the amount of generated heat became noticeable. In tests by Walker and Harrison (1977) the rate of self-heating increased with temperature, as did the rate of pyrolysis. In most of these mentioned experiments, wood probably released heat before the investigators detected it.

Heat release is reflected by the temperatures of samples, but these depend also on heat loss. The smallest samples lose the highest proportions of generated heat, since the material generates heat in proportion to its volume, whereas the heat dissipates in proportion to the surface area. For a sphere, for example, the ratio of volume ($4/_3\pi r^3$) to surface area ($4\pi r^2$) increases in proportion to the radius (r).

Large samples heat up unevenly, so that heat released in a slowly decomposing layer is absorbed by an adjoining layer still too cold for pyrolysis, or else rapid endothermic pyrolysis in an adjoining hotter layer disguises the release. In rapidly heated small samples, the exothermic phase is too short and passes unnoticed. Hence heating tests at rapidly changing temperatures fail to show the thermal balance.

Differential thermal analysis trials cannot reveal realistic thermal balances for another reason. In the samples, typically weighing only a fraction of one gram, the pyrolysis products have little opportunity to interact and to evolve in stable forms. Exothermic points observed in trials of this kind are therefore relatively high and erratic (MacKay 1967), which should not be surprising, at least not when the temperatures in the tests rose at relatively rapid rates of 5 to 10 C/min (MacKay 1967).

Constant-temperature pyrolysis trials with large samples appear best suited for detecting the thermal balance. The difficulty with them lies in detecting the small amount of heat given off during any particular period of time. The heat may be significant in total, but it evolves slowly.

Much of or even all heat generated by so-called smoldering combustion may be heat of pyrolysis. The absence of flames above the smoldering material indicates that the evolving volatiles do not burn, though the charred residue may react with oxygen at the surface. In many cases the char seems too cool for combustion; otherwise combustion would raise the temperature, in this way accelerating pyrolysis as well as combustion itself, and the hot glowing char would ignite the volatiles.

Wood in structures occasionally self-heats and ignites after many months or years of exposure to the constant heat between 80 and 150 C of steam pipes and other hot items (Matson et al. 1959). The findings of this study explain the phenomenon: when pyrolysis of hot wood slows down as time passes, it becomes more exothermic and reaches a point at which more heat is generated than can dissipate into the surroundings. The material self-heats because of slow pyrolysis so that the temperature rises to levels of oxidation and ignition.

Little can be done against pyrolytic self-heating in the field. Exclusion of air—for example by covering the pile with sheets of plastic film—has no effect since pyrolysis does not consume oxygen. Injected water cools the material by absorbing heat; but in dry material, the injected water may also generate heat of wetting and of hydrolysis. Water furthermore devalues the products. Self-heating processes that precede pyrolysis (respiration of wood cells and metabolism of microorganisms) are easier to control inasmuch as they depend on oxygen, re-

spond to biocides, and are slow by nature, regulating themselves as rising temperatures kill cells and organisms. Therefore pyrolytic self-heating should be prevented early by cooling the material, for example by opening piles of wood chips and by unstacking hot boards, but doing so before such opening can cause rapid oxidation and ignition.

REFERENCES

AARON, J. R. 1980. The production of wood charcoal in Great Britain. Forest Report No. 121. Gr. Brit. Forestry Comm., London, GB.

BERGMAN, O. 1974. Thermal degradation and spontaneous ignition in outdoor chip storage. Sven. Paperstidn. 77(18):681–684.

BROWNE, F. L. 1958. Theories of the combustion of wood and its control. For. Prod. Lab. Rep. No. 2136. For. Prod. Lab., Madison, WI.

——, AND J. J. BRENDEN. 1964. Heat of combustion of the volatile pyrolysis products of fire-retardant-treated ponderosa pine. U.S. Forest Service Res. Paper FPL 19. For. Prod. Lab., Madison, WI.

DEMIDOV, P. G. 1962. Combustion and properties of combustible substance. Izdatel'stvo Ministerstva Kommunal'nogo Khozyaystva RSFSR, Moscow.

GOOS, A. W. ET AL. 1948. Some experiments in sawdust carbonization. Proc. For. Prod. Res. Soc. 2:55–59.

HEINRICH, H. J., AND B. KAESCHE-KIRSCHER. 1962. Contribution to research on spontaneous heating of wood. Brennstoff-Chemie 43(5):142–148.

HOLMGREN, B. 1948. Self-ignition of porous wood fiberboard. Sven. Paperstidn. 51(10):230–232.

JACH, W. 1973. State of the art on research about biological self-heating. 4. International Fire Protection Seminar 1973 Zurich. Brand-Verhutungs-Dienst fur Industrie und Gewerbe, Zurich, Switzerland.

KLASON, P. 1914. Theory for dry distillation of wood. J. Praktische Chemie B90(10+11):413–447.

—— ET AL. 1909. Dry distillation of cellulose. Zeitschr. Angew. Chemie 22(25):1205–1214.

—— ET AL. 1910. Dry distillation of pine, spruce, birch, and beech wood. Zeitschr. Angew. Chemie 23(27):1252–1257.

KOLLMANN, F. 1960. Occurrence of exothermic reactions in wood. Holz Roh- Werkst. 18(6):193–200.

MACKAY, G. D. 1967. Mechanism of thermal degradation of cellulose. Canada Dep. of For. and Rural Dev. Dep. Publ. No. 1201. Forestry Branch, Ottawa, Canada.

MATSON, A. F. ET AL. 1959. Survey of available information on ignition of wood exposed to temperatures. Bull. of Res. 51. Underwriters' Laboratories, Chicago, IL.

MESSNER, K., AND W. SERENTSCHY. 1978. Ecological factors and fungal flora in industrial piles of sawdust. Holzforsch. Holzverwert. 30(4):77–79.

MURPHY, E. S. 1962. Thermal decomposition of natural cellulose in vacuo. J. Polymer Sci. 58(166/1):649–665.

OSTLIN, B. 1959. Ignition of wood at temperatures below the normal ignition point. Sven. Paperstidn. 63(7):225–227.

PLATH, E., AND L. PLATH. 1955. Paper chromatography studies on European beech-steaming condensates. Holz Roh- Werkst. 13(6):226–236.

RILEY, R. G. 1979. Fires in raw material storage. Pulp Paper 53(14):100–103.

ROTHBAUM, H. P. 1963. Spontaneous combustion of hay. J. Appl. Chem. 13(July):291–302.

SCHAFFER, E. L. 1966. Review of information related to the charring rate of wood. U.S. For. Serv. Res. Note FPL-0145. For. Prod. Lab., Madison, WI.

——. 1979. Smoldering combustion tendency. Thermal Insulation 2(1):135–140.

SPRINGER, E. L. ET AL. 1971. Spontaneous heating in piled wood chips. Tappi 54(4):589–591.

TSUCHIYA, Y., AND K. SUMI. 1977. Spontaneous ignition. Can. Build. Dig. 189:1–4.

WALKER, I. K., AND W. J. HARRISON. 1977. Self-heating of wet wood. New Zealand J. Sci. 20(2):191–200.

WIDELL, T. 1948. Thermal investigation into carbonization of wood. The Royal Swedish Academy of Engineering Sciences, Proc. No. 199. Generalstabens Litografiska Anstalts Forlag, Stockholm, Sweden.