

# THERMOGRAVIMETRIC ANALYSIS OF WOOD LIGNIN AND HEMICELLULOSES

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## ABSTRACT

Dynamic thermogravimetric analysis was performed on five forms of lignin and nine preparations of hardwood and softwood hemicelluloses. Kinetic parameters were determined for pyrolysis and combustion in nitrogen and oxygen over 25 to 1000 C at 6 C/min. The weight loss data were analyzed for activation energies assuming zero and first order decomposition with an Arrhenius behavior. Lignin stability appeared related to preparation and molecular weight, with sulfuric acid as the least representative of protolignin behavior. Softwood and hardwood hemicelluloses degraded characteristically. Softwood compression wood galactan degraded catastrophically during the combustion analysis.

An understanding of the thermal degradation characteristics of wood and wood components can help in developing and implementing methods to improve the fire performance of wood. Pyrolysis, the thermal degradation of a material in an inert atmosphere, provides information on the generation of gaseous products. Combustion is closely related to pyrolysis in that the gaseous pyrolytic products mix with oxygen, promoting flaming or glowing. Degradation during pyrolysis was the method formerly used to obtain useful chemical products from wood. Recent research in wood pyrolysis is concentrated on exploring the thermal properties under controlled conditions, and these results are used to understand or modify the fire performance characteristics of wood.

Thermogravimetric analysis (TGA) is one of the techniques used to determine general degradation characteristics and activation energies of materials under pyrolysis and combustion. This analysis includes a precise study of weight loss during programmed exposure to temperature.

## STRUCTURE AND THERMAL BEHAVIOR

The structural components of wood include cellulose, hemicelluloses, and lignin.

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Since cellulose is the major component of wood, paper, and cotton, its degradation properties have been intensively studied. Lignin and the hemicelluloses comprise about 60% of wood, but have received little attention.

## Lignin

Lignin is an insoluble, amorphous polymer composed of highly crosslinked phenylpropanoid units. Softwoods contain between 25 and 35% of a fairly homogeneous lignin, while hardwoods have 18 to 25% of a more variable lignin (Pearl 1967). About 75% of the lignin in wood is found within the cell walls, with the remainder in the middle lamella (Côté, Day, and Timell 1968).

Little information is available on lignin TGA. Tang (1967) found two stages of first-order decomposition for sulfuric-acid spruce lignin, 280–344 C and 344–435 C, with activation energies of 21 and 9 kcal/mole, respectively. The study was conducted *in vacuo* at 3 C/min with 100 mg samples. In a long-term weight loss study at 150 C in an oven, Stamm (1956) found that Klason lignin degraded at one-half the rate of wood. The activation energy for lignin degradation between 110 and 220 C was 23 kcal/mole.

Other studies using different methods of analysis have produced related results. Domansky and Rendos (1962) compared the DTA curves of different acid lignin prepattern was practically the same for each.

Kudo and Yoshida (1957) analyzed dry-distilled wood samples for methoxyl group

content after isothermal heating at temperatures between 150 and 500 C. They proposed that lignin decomposition begins at about 280 C with a maximum rate occurring between 350 and 450 C, and completion of the reaction at 450–500 C.

Kollmann and Fengel (1965) found that lignin had the greatest stability of all wood components in thermal treatments below 200 C. Between 100 and 150 C, the hydrolysis-resistant compounds of oak decompose, causing a decrease in lignin content. Pine lignin content, however, remained constant over this temperature range. About 150 C, the lignin content of both oak and pine increased, presumably because of chemical reaction of the decomposed hemicelluloses with lignin.

Ramiah and Goring (1967) obtained decomposition activation energies of 52 and 108 kcal/mole for dioxane and periodate lignin, respectively. Dioxane lignin began decomposing at 130 C; the periodate lignin began decomposing at 145 C. The thermal stability of lignin was considered greater than that of the hemicelluloses and less than that of cellulose.

#### *Hemicelluloses*

The hemicelluloses consist of the non-cellulosic polysaccharides. In contrast with the high crystallinity and linearity of cellulose, hemicelluloses are largely noncrystalline and slightly branched. Hemicelluloses differ between softwoods and hardwoods, and among species in each group (Timell 1967).

*Structure.*—In hardwoods, a partially acetylated acidic xylan, *O*-acetyl-4-*O*-methylglucuronoxylan, comprises 20 to 35% of the wood substance. It can be extracted (from the holocellulose obtained after chlorite delignification) with DMSO and water in quantities of up to 50%. The non-acetyl form can be directly removed from wood in 70–80% yield with aqueous KOH. Deacetylation in extraction causes a loss of water solubility. The acetylated form may contain about 16% acetyl groups on a slightly branched backbone of up to 200 xylan residues. A glucomannan present to

the extent of 3 to 5% in hardwoods consists of glucose and mannose residues in a ratio of 1:2 except in *Betula*, where the ratio is 1:1. Because of degradation during extraction, most molecular properties of the native material are unknown.

Two extractable fractions of galactoglucomannan hemicelluloses predominate in softwoods. The water-soluble fraction comprises 5–10% of the wood and has galactose:glucose:mannose residues in a 1:1:3 ratio. The alkali-soluble fraction, 10–15% of the wood, has a 0.1:1:3 residue ratio. The mannose residues are probably acetylated in the native state. The backbone contains a minimum of 150 hexose residues. Branching appears to be slight or nonexistent. Softwoods also contain 10–15% of a xylan, arabino-4-*O*-methylglucuronoxylan, which differs primarily from hardwood xylan in having arabinofuranose residues. Little is known of its native physical structure.

Compression wood in softwoods contains 10 to 12% of a galactan with galactopyranose residues. *Picea abies* and *Picea rubens* galactan contain uronic acid residues which may not be structurally incorporated in the native state.

Arabinogalactan found in *Larix* is highly branched, water-soluble, and composed of two similar fractions of different molecular weights. It is a non-structural hemicellulose found primarily in extracellular deposits in heartwood.

*Thermal behavior.*—The thermal characteristics of wood hemicelluloses have not been studied in depth, partly because of the former lack of satisfactory isolation techniques. Kudo and Yoshida (1957) found that both natural extractives and hemicelluloses decompose above 150 C with a 280 C limit of hemicellulose decomposition. Minami and Kawamura (1958) concluded that *Quercus glauca* hemicelluloses decomposed similarly whether isolated or *in situ*. Domansky and Rendos (1962) isolated hemicelluloses from birch, spruce, poplar, and maple and found them to be the thermally least stable wood components. This instability, relative to cellulose, was proposed to be caused by the amorphous struc-

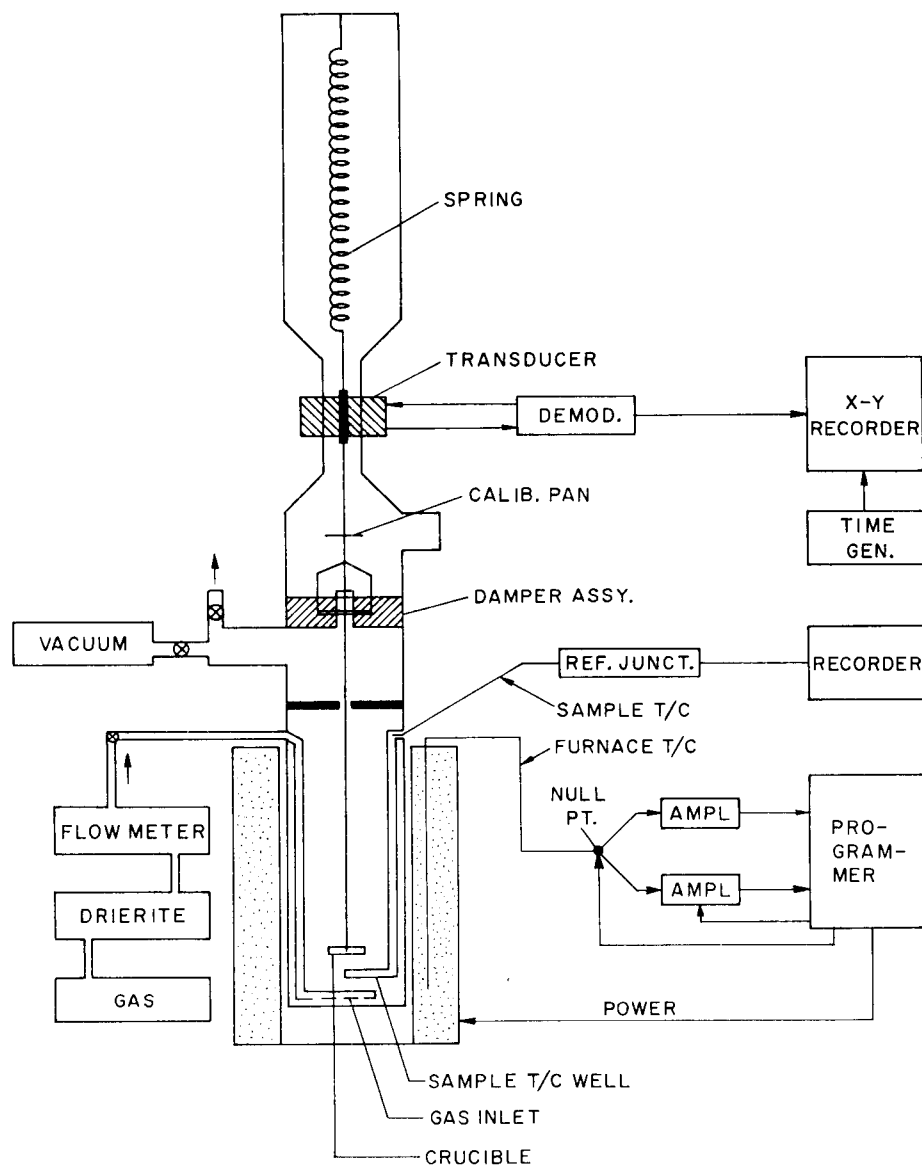


FIG. 1. Schematic diagram of American Instrument Co. "Thermograv" and associated equipment.

ture of the hemicelluloses. According to Kollmann and Fengel (1965), cellulose stability is reduced because of the interaction with hemicelluloses. The apparent hemicellulose content remained constant between 150 and 180 C because of fragmentation of cellulose into hexosan units, which then appeared as part of the hemicellulose fraction. This was subsequently

studied in detail and confirmed by Fengel (1966b). Fengel (1966a) proposed a two-stage decomposition for hemicelluloses: (a) fragmentation into water-soluble molecules followed by (b) either a depolymerization of the short, fragmented chains to the monomer and volatilization, or a rapid direct degradation to volatiles without observable monomeric fragments.

TABLE 1. *Lignin physical and chemical characteristics*

Type <sup>a</sup>	Preparation method	Molecular weight (Wt. avg.) <sup>b</sup>	Carbohydrate content (%)
Björkman	Dioxane extraction (Browning 1967)	11,000	0.2
Brownell	NaCNS extraction (Brownell 1965)	13,700	4.5
Sulfuric acid	H <sub>2</sub> SO <sub>4</sub> (72%) extraction (Browning 1967)	— <sup>c</sup>	0
Cellulase	Enzymatic degradation (Pew 1957)	25,400	6.0
DHP	Enzymatic synthesis (Kratzl 1965)	20,000	NA

<sup>a</sup> All samples except the sulfuric acid type were obtained through the courtesy of Dr. J. M. Harkin, Forest Products Laboratory.

<sup>b</sup> By ultracentrifugation, dioxane solvent.

<sup>c</sup> Not soluble in dioxane.

Domburg, Sergeeva, Kalminsh, and Kiselis (1966) found that isolated xylan degrades differently in an inert atmosphere than *in vacuo*. Under atmospheric pressure, fragmentation occurs between about 225–300 C, followed by dehydration and furfural production. Beyond 300 C, a graphitic structure results from secondary reactions. In a vacuum, cross linking of fragments apparently prevents furfural production. Anhydride compounds are formed and evaporate between about 220–300 C.

In a gas evolution study, Ramiah and Goring (1967) obtained an activation energy of 46 kcal/mole for the decomposition of birch xylan which began at 117 C. Pine glucomannan began a first-order decomposition at 127 C and was presumed more stable because of its partial crystallinity. They concluded that the hemicelluloses were the least stable wood components.

#### MATERIALS AND PROCEDURES

The dynamic TGA was performed with an American Instrument Company thermo-

gravimetric balance shown schematically in Fig. 1 with the associated equipment. The sample was suspended from an assembly consisting of phosphor-bronze springs attached to a rod holding a transducer core and damping assembly. The sample crucible and crucible support were connected to the lower end of the rod. A flat stainless steel crucible was used instead of a standard ceramic crucible, minimizing effluent gas diffusion by increasing the sample surface-to-volume ratio.

The types of lignin used in this study are listed in Table 1. DHP lignin is a synthetic lignin which displays most of the characteristics associated with "natural" lignin. Because all of the nonsynthetic lignins were removed from spruce (*Picea* sp.), the protolignin was considered to have been identical. Table 2 lists the hemicelluloses used in this study. Two commercial hemicelluloses, xylan and arabinogalactan, were included for comparison with the much more refined laboratory samples. Tension wood galactan was not available in sufficient quantity for testing and has not been

TABLE 2. *Hemicellulose types and sources*

Type	Source <sup>a</sup>
O-acetyl-4-O-methylglucuronoxylan	<i>Betula papyrifera</i> Marsh.
4-O-methylglucuronoxylan	<i>Betula alleghaniensis</i> Britton
Xylan	Nutritional Biochemicals Corp.
Galactoglucomannan (0.1 : 1 : 3)	<i>Pinus strobus</i> L.
Galactoglucomannan (1 : 1 : 3)	<i>Tsuga canadensis</i> (L.) Carr.
Arabino-4-O-methylglucuronoxylan	<i>Tsuga canadensis</i> (L.) Carr.
Galactan (compression wood)	<i>Abies balsamea</i> (L.) Mill
Arabinogalactan	<i>Larix laricina</i> (Du Roi) K. Koch
Arabinogalactan (STRactan AF#2)	Stein, Hall & Co., Inc.

<sup>a</sup> All samples indicated by wood species were high purity preparations obtained through the courtesy of Dr. T. E. Timell, State University of New York College of Forestry at Syracuse.

discussed in this study. Hardwood glucmannan also was not available in sufficient quantity or quality.

Weight versus time (w vs. t) was plotted on the internal X-Y recorder, using the transducer output to provide Y-axis data, and an internal time generator for the X-axis position. A strip-chart recorder was used to plot the sample thermocouple emf against time. The w vs. t curves were digitized at 1-min intervals, while the emf-time curves were analyzed for the rate of heating over a selected temperature interval. Corrections were made for effects of buoyancy on the apparent weight and for the lag of the sample crucible temperature with the recorded temperature. The rate of weight change ( $\dot{w}$ ) was determined by the change in weight at the 1-min intervals.

The kinetics were evaluated by differential-difference methods (Flynn and Wall 1966) using the following general equation:

$$-\dot{w} = kw^n, \quad (1)$$

where  $\dot{w}$  = rate of weight change (mg/min),  $w$  = mass (mg),  $t$  = time (min),  $n$  = order of reaction,  $k$  = reaction constant.

The temperature dependence of Equation 1 was assumed to follow the Arrhenius equation:

$$k = Ae^{-E/RT} \quad (2)$$

Where  $A$  = pre-exponential constant,  $E$  = apparent activation energy (cal/mole),  $R$  = gas constant (cal/mole-K),  $T$  = temperature (K). Combining Equations 1 and 2,

$$-\dot{w} = Ae^{-E/RT}w^n. \quad (3)$$

After taking the logarithm and rearranging,

$$\ln(-\dot{w}/w^n) = \ln(A) - E/RT. \quad (4)$$

Activation energy may then be found from the slope of the  $\ln(-\dot{w}/w^n)$  versus  $1/RT$  curve.

Methods are available to analyze the order of reaction ( $n$ ), but many of these lead to less accurate data because of assumptions used to obtain the final expression. In most studies on wood components, an integer order of reaction, 0 or 1, has been assumed to allow a meaningful comparison

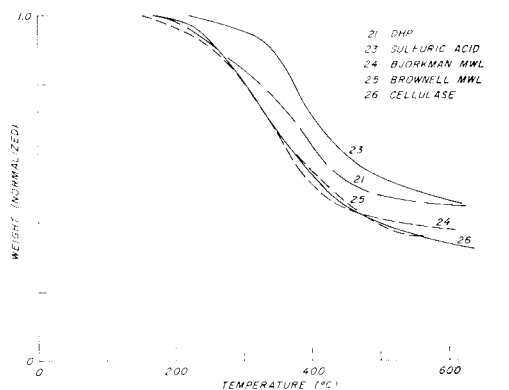


FIG. 2. TGA pyrolysis of different lignin forms heated in nitrogen at 6 C/min.

of activation energies among these studies. However, if the order of reaction is independently determined, the comparison between studies is valid only if the same order of reaction had been assumed. For these reasons, the data were analyzed for zero- or first-order behavior with a least-squares criterion.

## RESULTS AND DISCUSSION

### *Lignin Pyrolysis*

The pyrolytic degradation of the lignins listed in Table 1 is shown in Fig. 2, omitting the slow weight loss between 700 and 1000 C. The Brownell and cellulase lignins correlated best, possibly because of their relatively high carbohydrate contents. Sulfuric acid lignin was the most stable and apparently the least representative because of the absence of low molecular weight molecules and its high degree of molecular condensation. DHP lignin followed a different degradation path from those of the others, particularly between 10 and 20% weight loss. The lack of accelerated degradation of DHP lignin near the point of 10% weight loss may reflect the structural integrity of DHP as compared with the others, all of which had been milled before lignin extraction. The lignin molecular weights given in Table 1 correlated well with the initial weight loss showing an increase of thermal stability with molecular weight.

TABLE 3. Kinetic behavior of 50-mg samples of lignin during pyrolysis in nitrogen and combustion in oxygen at 6 C/min.

Lignin type	Reaction <sup>a</sup>	Activation energy (kcal/mole)	Temperature range (C)	Maximum rate of wt. loss <sup>b</sup> (mg/min)	Temperature at maximum rate of wt. loss <sup>b</sup> (C)	Decomposition temperature <sup>c</sup> (C)	
						10%	50%
Brownell	P	(0) <sup>d</sup> 6.0 ± 8%	175-245	0.6	303	241	366
		(1) 6.7 ± 5%	175-310				
	C	(0) 5.8 ± 5%	167-203	1.5	353	254	356
		(1) 18.2 ± 10%	214-249				
Björkman	P	(0) 8.0 ± 2%	185-245	0.8	363	228	358
		(1) 9.0 ± 4%	250-330				
	C	(0) 15.2 ± 3%	187-234	1.2	429	273	407
		(1) 6.2 ± 10%	266-388				
Sulfuric acid	P	(0) 8.6 ± 0%	260-325	0.8	381	331	428
		(1) 11.1 ± 7%	235-325				
	C	(0, 1) 18.1 ± 2%	315-375	1.9	432	293	392
		(0) 24.3 ± 12%	219-254				
Cellulase	P	(0) 10.7 ± 7%	178-239	0.7	297	266	367
		(1) 5.6 ± 8%	260-300				
	C	(0) 17.4 ± 1%	185-236	1.4	414	261	372
		(1) 7.4 ± 6%	322-384				
DHP	P	(0) 2.0 ± 30%	220-340	0.7	390	254	391
		(1) 4.1 ± 2%	195-330				
	C	(1) 9.3 ± 5%	335-385	2.9	444	287	451
		(1) 6.5 ± 9%	170-337				
		(0) 15.3 ± 20%	337-404				
		(1) 32.9 ± 2%	398-439				

<sup>a</sup> P = pyrolysis; C = combustion.

<sup>b</sup> Pre-ignition values for combustion.

<sup>c</sup> Number indicates per cent decomposable weight loss.

<sup>d</sup> Number enclosed in parentheses is order of reaction.

The pyrolysis kinetic behavior shown in Table 3 was derived from Fig. 2 and shows numerically the relationship among the lignins. All lignins except the Brownell type followed a two-step degradation. DHP and sulfuric acid lignins followed zero- and first-order degradation paths equally well in the initial step. Brownell lignin followed first-order degradation over a greater range of temperature than any other lignin.

The results in this study for the pyrolysis of sulfuric acid lignin conflict with those of Tang (1967) who found decreasing activation energies (21 to 9 kcal/mole as compared with 11 to 18 in this study) with

increasing temperature. In all other studies, either an entirely different method of analysis was used, or isothermal conditions were maintained.

#### Lignin Combustion

Fig. 3 and Table 3 show the thermograms and kinetic data for the combustion of the lignins. Ignition occurred in all samples except sulfuric acid lignin near 70 to 80% decomposition. The maximum rate of decomposition occurred just before ignition (excluding that occurring during ignition), permitting a complete kinetic analysis. The maximum rates in Table 3 were higher for

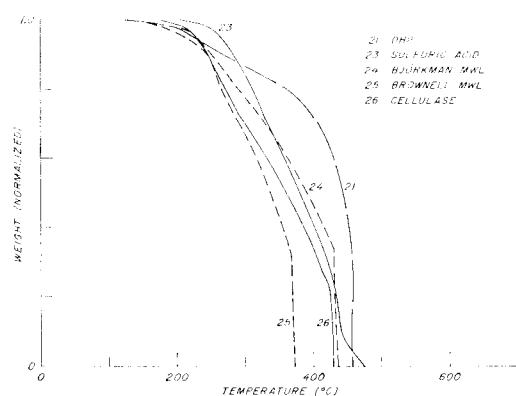


FIG. 3. TGA combustion of different lignin forms heated in oxygen at 6 C/min.

combustion than for pyrolysis, with the greatest change in DHP lignin. Each type of lignin followed a three-step decomposition in oxygen.

DHP lignin apparently reacted with molecular oxygen, forming new bonds that increased the thermal stability during the initial decomposition phase. Björkman, Brownell, and cellulase lignins decomposed similarly when compared with sulfuric acid or DHP lignins. DHP lignin followed the reverse of the 0 to 1 kinetic order sequence

found for other lignins. Cellulase and Björkman lignins were the most similar in kinetic sequence and magnitude of activation energies. Both sulfuric acid and DHP lignin appeared nonrepresentative in their degradation during combustion.

#### Hardwood Hemicellulose Pyrolysis

Table 4 shows the kinetic data for hardwood hemicelluloses derived from Figs. 4 and 5. The pyrolytic thermal stabilities were greater for the samples having a higher degree of degradation from extraction, with native and commercial xylans the least and most stable, respectively. Native xylan also had a considerably higher rate of decomposition than the others: the native xylan had lost about 50% of its decomposable weight when the physically degraded forms had lost only 10%. At least part of this high weight loss can be attributed to the acetyl groups which probably have been lost by this time. All three samples degraded to approximately the same final mass, implying a similar final structure. Native xylan degraded at a similar rate for either reaction order over the complete range, while the others followed two-step, 0-1 order sequences. The higher activation energy of

TABLE 4. Kinetic behavior of 50-mg samples of hardwood xylan during pyrolysis in nitrogen and combustion in oxygen at 6 C/min.

Hardwood xylan type	Reaction <sup>a</sup>	Activation energy (kcal/mole)	Temperature range (C)	Maximum rate of wt. loss <sup>b</sup> (mg/min)	Temperature at maximum rate of wt. loss <sup>b</sup> (C)	Decomposition temperature <sup>c</sup> (C)	
						10%	50%
Native	P	(0) <sup>d</sup> 41.0 ± 2%	210-245	4.5	254	216	265
		(1) 39.4 ± 10%	195-250				
	C	(0) 51.2 ± 2%	211-233	5.3	238	233	264
		(1) 39.0 ± 7%	238-257				
Deacetylated	P	(0) 25.5 ± 20%	227-245	3.4	283	248	292
		(1) 18.0 ± 3%	250-280				
	C	(0) 57.4 ± 20%	208-230	9.2	236	242	254
Commercial grade	P	(0) 15.7 ± 10%	215-245	3.5	290	256	298
		(1) 23.4 ± 5%	245-285				
	C	(0) 25.7 ± 4%	193-225	5.9	246	236	263
		(1) 39.3 ± 6%	222-246				

<sup>a</sup> P = pyrolysis; C = combustion.

<sup>b</sup> Pre-ignition values for combustion.

<sup>c</sup> Number indicates per cent decomposable weight loss.

<sup>d</sup> Number enclosed in parentheses is order of reaction.

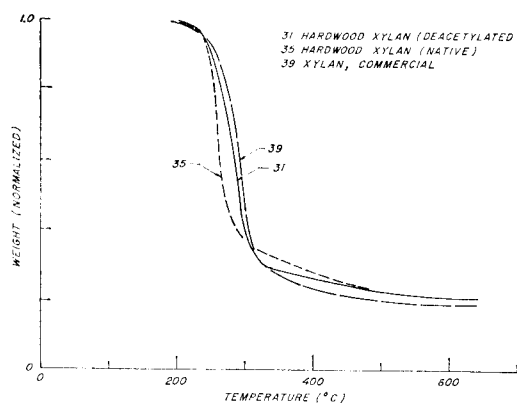


FIG. 4. TGA pyrolysis of hardwood xylans heated in nitrogen at 6 C/min.

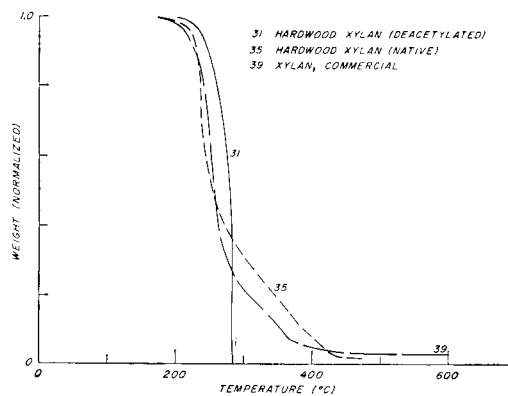


FIG. 5. TGA combustion of hardwood xylans heated in oxygen at 6 C/min.

native xylan may have resulted from hydrolysis of acetyl groups. Differences between activation energies of the zero-order stages for the degraded xylans may have been caused by the more degraded state or higher degree of impurities of the commercial xylan.

#### Hardwood Hemicellulose Combustion

The differences among the hardwood xylan samples are even more evident in combustion than in pyrolysis. Fig. 5 shows that the combustion degradation of deacetylated xylan (sample 31) and of native xylan (sample 53) to 50% residual weight followed nearly the same path as it did during pyrolysis (Fig. 4), although at lower temperatures. Even though the native xylan decomposed more rapidly in oxygen, ignition of the sample did not occur. In contrast, the deacetylated xylan ignited near the 50% weight-loss temperature. The behavior of the commercial xylan sample was completely different in oxygen; it showed less stability than the deacetylated xylan, the reverse of the result with pyrolysis. The deacetylated hardwood xylan deviated more than the other hardwood xylans with respect to its kinetic behavior in oxygen as compared with nitrogen. Native hardwood xylan showed little difference in the activation energies obtained during degradation in oxygen or nitrogen in the same region. The commercial xylan reacted similarly,

but with a slightly higher activation energy in oxygen for the two-step decomposition.

#### Softwood Hemicellulose Pyrolysis

The TGA degradation curves for softwood cell-wall hemicelluloses are shown in Figs. 6 and 7. The order of increasing quantity of each of these hemicelluloses in softwoods free of compression wood is: galactoglucomannan (0.1:1:3) and xylan, 10–15%; and galactoglucomannan (1:1:3), 5–10%. Galactan from compression wood produced degradation curves markedly different from those of other hemicelluloses. It degraded at the highest temperature, reached its maximum rate of decomposition also at the highest temperature, and left the lowest

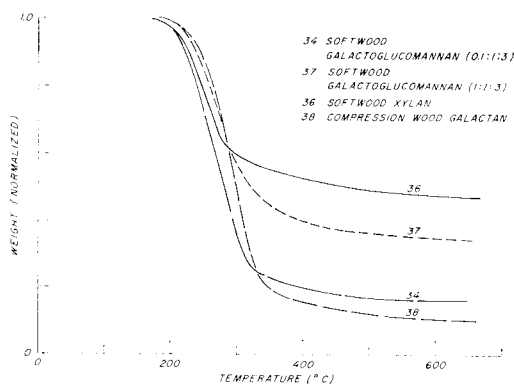


FIG. 6. TGA pyrolysis of softwood hemicelluloses heated in nitrogen at 6 C/min.



TABLE 5. Kinetic behavior of 50-mg samples of softwood hemicelluloses during pyrolysis in nitrogen and combustion in oxygen at 6 C/min.

Softwood hemicellulose	Reaction <sup>a</sup>	Activation energy (kcal/mole)	Temperature range (C)	Maximum rate of wt. loss <sup>b</sup> (mg/min)	Temperature at maximum rate of wt. loss <sup>b</sup> (C)	Decomposition temperature <sup>c</sup> (C)	
						10%	50%
Galactoglucomannan (0.1 : 1 : 3) <sup>e</sup>	P	(0) <sup>d</sup> 31.6 ± 15%	180–196	1.9	291	223	277
		(0,1) 22.1 ± 5%	196–212				
		(1) 7.8 ± 7%	225–285				
Galactoglucomannan (1 : 1 : 3) <sup>e</sup>	C	(0) 25.0 ± 3%	175–213	3.0	238	218	258
		(0) 21.3 ± 20%	207–235				
		(1) 8.8 ± 20%	238–278				
Xylan	P	(0) 32.5 ± 4%	196–227	1.6	279	238	293
		(1) 27.5 ± 10%	199–232				
		(0) 22.2 ± 4%	190–217				
Compression wood galactan	C	(1) 3.4 ± 20%	240–250	1.4	249	218	265
		(0) 43.5 ± 5%	178–198				
		(1) 20.2 ± 2%	197–213				
Arabinogalactan (native)	P	(0) 17.9 ± 7%	192–247	2.3	302	249	303
		(1) 10.3 ± 10%	247–285				
		(1) 16.9 ± 1%	280–301				
Arabinogalactan (commercial grade)	C	(0) 42.9 ± 7%	180–195	—	200	—	—
		(0) 29.5 ± 1%	225–245				
		(1) 29.3 ± 2%	275–305				
Arabinogalactan (commercial grade)	P	(0) 29.0 ± 2%	220–242	3.6	305	260	305
		(1) 31.0 ± 10%	234–272				
		(0) 43.3 ± 1%	190–200				
Arabinogalactan (commercial grade)	C	(1) 7.3 ± 6%	220–255	4.3	298	240	303
		(1) 39.2 ± 12%	270–290				
		(1) 13.8 ± 6%	183–252				
		(1) 32.2 ± 12%	252–286	3.2	286	244	308

<sup>a</sup> P = pyrolysis; C = combustion.<sup>b</sup> Pre-ignition values for combustion.<sup>c</sup> Number indicates per cent decomposable weight loss.<sup>d</sup> Number enclosed in parentheses is order of reaction.<sup>e</sup> Ratio of galactose:glucose:mannose residues.

quantity of residue. The compression wood galactan is a linear polymer which probably accounts for its similarity to cellulose (Fig. 10) with respect to decomposition behavior. The xylan from normal softwood, on the other extreme, degraded slowest, reached the maximum decomposition rate at the lowest temperature, and left the greatest quantity of residue of all the softwood hemicelluloses. The 0.1:1:3 galactoglucomannan from normal softwood behaved similarly to the compression wood galactan, but degraded at a somewhat lower temperature.

The primary difference between the

galactoglucomannans is the number of  $\beta$ -D-galactopyranose residues present as side groups attached to the backbone (0.1 for sample 34 and 1 for sample 37, compared with 1  $\beta$ -D-glucopyranose and 3  $\beta$ -D-mannopyranose residues in the backbone). Sample 34 is more like a polymer without side groups, such as the compression wood galactan, and degraded similarly. The extra side groups in the less abundant galactoglucomannan (1:1:3) apparently add to its thermal stability. Both galactoglucomannans are considered to be slightly branched (Timell 1967). The softwood xylan left an even greater residue than the lignins, but

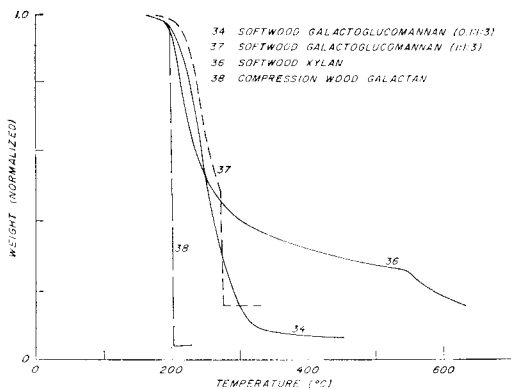


FIG. 7. TGA combustion of softwood hemicelluloses heated in oxygen at 6 C/min.

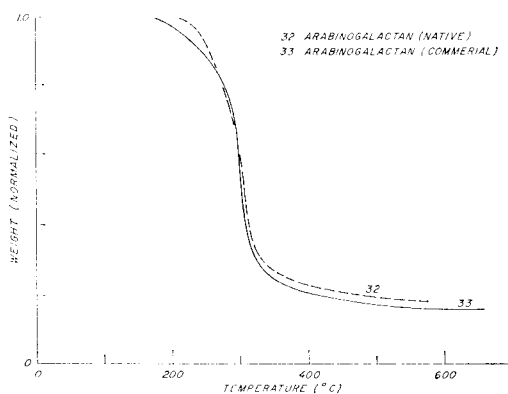


FIG. 8. TGA pyrolysis of larch arabinogalactan heated in nitrogen at 6 C/min.

the stability of this xylan in the later stages of decomposition is not readily apparent.

The zero- to first-order kinetic sequence behavior was also observed with the softwood cell-wall hemicelluloses. The glucomannans, although differing considerably from one another in the TGA curves, gave very similar activation energies in the same temperature ranges, with the second-step values less than one-half those of the first. The softwood xylan decomposed with the same energy requirement in the initial stage, but the second stage value was much lower than that of the galactoglucomannans. Compression wood galactan had a slightly lower activation energy than the glucomannans in the zero-order initial stage. In the last stage, however, up to the point of maximum decomposition, the activation energy was about double that of the galactoglucomannans.

#### *Softwood Hemicellulose Combustion*

Of the softwood hemicelluloses, only the xylan had not completely degraded at the upper temperature limit (Fig. 7). This hemicellulose also had the greatest residual weight after pyrolysis in nitrogen (Fig. 6); its combustion followed a path roughly similar to that of pyrolysis throughout most of the degradation. The galactoglucomannans (samples 34 and 37) reacted much differently during combustion, although up to 50% decomposition, their behavior was

similar to that during pyrolysis. The type with high galactose content (sample 37) ignited at about 50% decomposition. The other sample, No. 34, however, followed a smooth path until its residue was about half that of the pyrolysis residue. The weights of residues from all of the softwood hemicelluloses followed roughly the same sequence as they did in pyrolysis. It appears significant that the most prevalent hemicelluloses in softwoods, represented by samples 34 and 36, each degraded at a smooth rate during combustion.

Except for sample 34 (0.1:1:3 galactoglucomannan), the softwood hemicelluloses had higher initial activation energies during oxygen combustion, implying that oxidation processes were competing or interfering with volatilization. Softwood xylan (sample 36) and softwood glucomannan (1:1:3) (sample 37) again followed a zero-first order kinetic sequence, with lower activation energies in the second stages. Because of the early ignition of compression wood galactan, only a single value could be obtained for the activation energy. The behavior of this galactan during combustion followed that of cellulose very closely, as it did during pyrolysis.

#### *Arabinogalactan Pyrolysis and Combustion*

The differences between the behavior of arabinogalactans from various sources appear to be accentuated during combustion

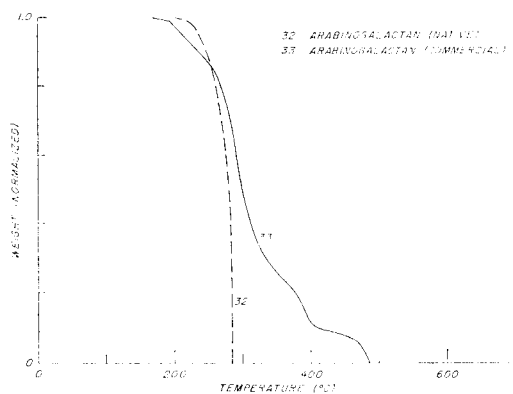


FIG. 9. TGA combustion of larch arabinogalactan heated in oxygen at 6 C/min.

(Fig. 9), as compared with pyrolysis (Fig. 8). The commercial material (sample 33) followed the same unusual initial behavior as in pyrolysis, to almost 20% weight loss. The native arabinogalactan, however, ignited and was completely consumed near the point of maximum rate of degradation. The commercial arabinogalactan followed a very complex path to complete degradation without ignition. The combustion of the commercial arabinogalactan and the hardwood xylan appeared similar, probably because of reaction of impurities generated in the extraction. Native arabinogalactan had a kinetic sequence in oxygen that was nearly identical with that of the pyrolysis sequence. The commercial arabinogalactan appeared to react somewhat similarly to pyrolysis in the second and third stages as is evident from a comparison of the values in Table 5.

#### Degradation Comparisons

In Fig. 10, curves for the various representative hemicelluloses are shown to compare hardwood and softwood types with the behavior of cellulose and of cellulase lignin. Hemicellulose (Nos. 34, 35, 36, 37) decomposition is nearly complete before accelerated degradation of cellulose (No. 11) occurs. The hardwood xylans (No. 35) decomposed similarly to cellulose at the start, whereas the softwood hemicelluloses (Nos. 34, 36, 37) appear to degrade some-

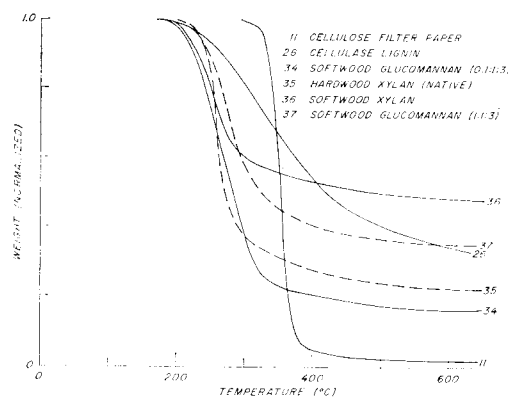


FIG. 10. TGA pyrolysis of representative wood components heated in nitrogen at 6 C/min.

what like lignin. All hemicelluloses decompose similarly in the final stage.

Most of the hemicelluloses behaved much differently when heated in oxygen. As expected, the initial degradation temperatures of hemicelluloses were lower in oxygen than in nitrogen and the maximum rates of degradation were higher in oxygen. Only sample No. 38, the compression wood galactan, ignited at an unusually low temperature during the degradation in oxygen. The degradation of compression wood galactan was too rapid to measure accurately. This behavior, combined with the low pyrolytic residue of this galactan, points out the need for further research on the behavior of compression wood under fire conditions.

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