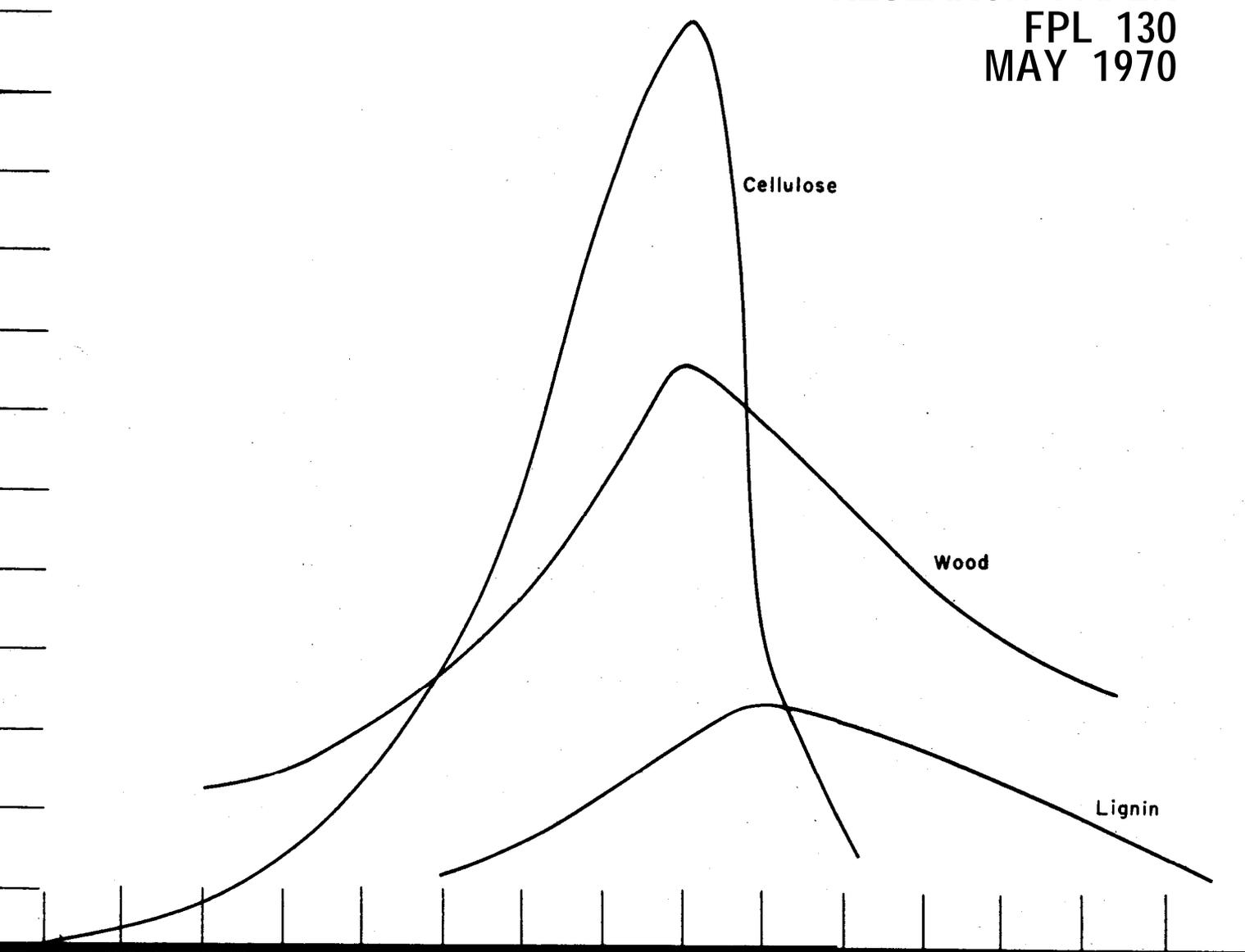


# THERMAL DEGRADATION OF WOOD COMPONENTS: a review of the literature

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## SUMMARY

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This review of literature was developed as part of an investigation to analyze the thermal degradation reactions of wood, cellulose, hemicelluloses, and lignin. Two methods are emphasized: Thermogravimetric analysis and differential thermal analysis. The process of general thermal degradation for wood is discussed and is followed by specific review of the literature on thermal analysis studies of wood and its components.

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# THERMAL DEGRADATION OF WOOD COMPONENTS: a review of the literature

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## INTRODUCTION

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This review of the literature was developed as part of an investigation of the thermal degradation analysis of wood and wood components (7).<sup>2</sup> The review was focused on thermal methods of analysis of the degradation of wood, cellulose, hemicelluloses, and lignin. The methods included thermogravimetric analysis (T G A) and differential thermal analysis (DTA). The use of relatively sophisticated thermal analysis equipment was begun about 1960. Prior to 1960, accurate continuous weight measurements were not available for TGA, and DTA lacked reasonable standards and commercial equipment. A few studies are included here for historical purposes; many earlier studies failed to meet present thermal analysis standards and are not included. This review of the literature was terminated in early 1968.

A discussion of the general thermal degradation process for wood is followed by a more specific review of the use of these methods to analyze the thermal degradation of wood and its components.

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## THERMAL DECOMPOSITION OF W O O D

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In reporting the exothermic reactions in wood, Kollmann (44) defined three phase points:

- (1) Flame point, 225° to 260° C., at which decomposition gases will burn if an ignition source is present.
- (2) Burning point, 260° to 290° C., at which burning occurs with a steady flame. (The decomposition becomes exothermic during the burning point and causes a self-induced flash.)
- (3) Flash point, 330° to 470° C., the range of spontaneous ignition.

Gillet and Urlings (27), in studying the decomposition of wood between 105° and 505° C. using isothermal heating in a nitrogen atmosphere, found active pyrolysis occurred near 250° to 260° C. In a subsequent study (28, 29), they concluded that the pyrolysis products of wood and of a cellulose-lignin mixture were the same above 450° C.

Hawley (33) defined the ignition temperature of wood as that temperature at which ignitable volatiles are produced even if a higher tempera-

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<sup>2</sup>Maintained at Madison, Wis., in cooperation with the University of Wisconsin.

<sup>3</sup>Underlined numbers in parentheses refer to Literature Cited at the end of this paper.

ture is required for ignition. The concept of a series of degradation zones was originated by Hawley and later modified by Browne (11).

Amy (3) describes the general course of pyrolysis of lignocellulosic materials. After the last traces of water are removed, which requires a temperature of about 140° C., four classes of products are produced by wood carbonization:

Noncondensable gases (carbon monoxide, carbon dioxide, hydrogen, methane).

Pyroligneous products (condensable, contain more than 50 percent moisture).

Tar (moisture-free, condensable).

Charcoal.

Gases are evolved at temperatures between 200° C. and 400° to 450° C., with a maximum at about 350° to 400° C. The rate of production of pyroligneous material passes through a maximum between 250° and 300° C. and virtually ceases at about 350° C. Tar forms between about 300° and 400° to 450° C. Some gases, primarily hydrogen, continue to be evolved above 400° C. Charcoal, which contains practically all the original ash, is not completely carbonized even at 1500° C.

The destructive distillation of wood has yielded up to 213 different compounds according to Goos (31). Some of these are from secondary reactions and processing.

While investigating dimensional stabilization, Seborg *et al.* (66) found both an overall volumetric decrease in the wood and a decrease in cell cavity volume. The greatest irreversible shrinkage effects occurred at the point equivalent to a 45 percent weight loss in a self-generated atmosphere, whereas a 60 percent weight loss in air resulted in an anti-shrinkage efficiency lower than that obtained in a self-generated atmosphere (atmospheric pressure) or in nitrogen. The darkening of wood heated in the dry condition or while submerged under molten metal after glycerin treatment to exclude air was interpreted as a thermal transformation in the absence of oxygen.

Mitchell *et al.* (54) studied the effect of heating Douglas-fir isothermally in a closed, pressurized system and in an open system with a static and a dynamic air or a nitrogen atmosphere. The closed system with a self-generated atmosphere produced the greatest weight loss. The data acquired in this study were later analyzed by Stamm (69).

The most comprehensive literature review to date on the thermal decomposition of wood was by

Browne (11), and covers pyrolysis, combustion, theories of flameproofing, fire-retardant ion mechanisms, and theories of glow prevention. He divides the pyrolysis processes into four zones, or temperature ranges, all of which can be present simultaneously in wood of appreciable thickness:

Zone A, below 200° C., in which only non-combustible gases, primarily water vapor, with traces of carbon dioxide, formic and acetic acids, and glyoxal are produced. Dehydration of sorbed water is complete.

Zone B, from 200° to 280° C. in which the same gases as in zone A are produced, but with a greatly reduced quantity of water vapor, and some carbon monoxide. At this point the reactions are endothermic, and the products are almost entirely nonflammable.

Zone C, from 280° to 500° C., in which active pyrolysis takes place under exothermic conditions leading to secondary reactions among the products. The products are largely combustible (carbon monoxide, methane, etc.), and include the highly flammable tars in the form of smoke particles. The charcoal residue catalyzes secondary reactions.

Zone D, above 500° C., in which the residue consists primarily of charcoal, which provides an extremely active site for further secondary reactions.

Early combustion stages are similar to the pyrolysis stages, modified slightly by oxidation. Using the same temperature zonal divisions as in pyrolysis, combustion may be categorized as follows:

Zone A, in addition to being characterized by the evolution of noncombustible gases, is affected by some exothermic oxidation processes.

Zone B, in which the primary exothermic reaction takes place without ignition. The ignition point, however, may also be defined as the temperature at which the exotherm begins.

Zone C, in which combustible gases that are ignitable are produced after secondary pyrolysis. Flaming combustion can then occur if the gases are ignited, but the flaming is restricted to the gas phase. If ignition is not induced, flaming may not occur until near the end of pyrolysis when the evolved gases cannot insulate the charcoal layer from oxygen. Spontaneous ignition of charcoal takes place at a temperature lower than any of the products evolved.

Zone D, above 500° C., the charcoal glows and is consumed. Above 1000° C., nonluminous flames are supported by the combustion of hydrogen and carbon monoxide.

Fengel (24) noticed certain anatomical changes in spruce heated at 180° and 200° C. The S-layer of summerwood tissue became fractured, and the encrusting materials in the torus began to flow at these temperatures, which also correspond to the transition temperature between zone A and zone B as defined by Browne (11).

### Thermal Analysis of Wood

Bamford *et al.* (6) investigated the problem of quantitatively expressing the rate of degradation of wood during combustion. They made trial decomposition runs and calculated an activation energy of 33.16 kilocalories per mole for wood decomposition, using a first-order equation. No data or experimental conditions were given in their report.

Wright and Hayward (74) studied the decomposition of dry western redcedar and western hemlock heated isothermally at 500°, 700°, and 900° C., in a static nitrogen atmosphere. The rate of decomposition was calculated from the pressure changes in the gases generated. The reaction rate was considered independent of any temperature gradient in the wood. A rate of reaction of the order one-half was observed; this correlated well with data that gave zero order reaction along the grain and two-thirds order across the grain. From this, it was concluded that the rate of reaction was independent of the chemical process, but dependent on the physical system. The basis of this experimental analysis has not been supported by other workers. Furthermore, the effect of the partial pressures of the self-generated atmosphere on the rate of generation of gases, which probably controlled the reaction direction and rate, was ignored.

Runkel and Wilke (6) investigated the chemical composition of beech and spruce after heating in a closed system. A steady carbohydrate (hemicellulose) decrease with temperature was found between 130° and 194° C. with the largest change above 180° C. The cellulose content remained unchanged in beech, whereas it decreased for spruce. The lignin content of both species ap-

parently increased at temperatures above 170° C., leading to the conclusion that polycondensates formed and added to the original lignin complex. This kind of an interaction between the hemicellulose and lignin fractions tends to support the theories of a close interrelationship in untreated wood.

A DTA study in air by Sergeeva and Vaivads (67) of air-dry birch and of certain wood components indicated that the interaction of wood components causes non-additive effects. The most characteristic reaction above 400° C. was from lignin decomposition. The peaks exhibited by cellulose, xylan, and hemicellulose were considered distinguishable in the wood thermogram. In previous work by Sergeeva (unpublished), non-additive effects of wood component decomposition had been observed in hydrogen reduction.

Akita (1) proposed a first-order kinetic equation involving the summation of the decomposition rates of the individual wood components

$$\frac{dw}{dt} = \sum_i k_i (w_{f_i} - w_i)$$

where  $w_f$  = final weight

$w$  = weight at time  $t$

A two-step decomposition was found to occur for wood on the basis of the Arrhenius equation with a transition temperature between steps at about 340° C. When isolated wood components were recombined and tested, the thermal reaction appeared the same as that for natural wood.

The thermal degradation of wood while heated in an air oven and while submerged in molten metal was found to fit a first-order reaction by Stamm (69). The activation energy of Douglas-fir sawdust was 25 kilocalories per mole when oven-heated in air at atmospheric pressure for a temperature range of 110° to 220° C. Other softwoods in the form of sticks and veneer gave an average activation energy of about 29.6 kilocalories per mole for both oven-heating and heating under molten metal for a slightly broader temperature range. Various wood components were found to have activation energies almost equal to those of wood. The conclusions reached were that greater degradation occurs (1) in air because of oxidation, (2) in a closed nonvented system because of acid accumulation and result-

ing hydrolysis, and (3) under conditions of high relative humidity.

Iskhakov ( 37 ) found the DTA thermogram of pyrolyzed. beech in nitrogen was almost independent of the rate of heating for the range from 2.2° to 16° C. per minute. Magnesium oxide was found to be a better reference standard than coke that exhibited endothermic and exothermic effects.

Wood samples were dynamically heated at about 0.3° C. per minute to pre-selected temperatures between 150° and 500° C. by Kudo and Yoshida ( 46 ). Each sample was removed and analyzed for ash, ether and 1 percent sodium hydroxide extractives, reduced sugar yield, and methoxyl groups. From the change in chemical composition, the temperature range for the decomposition of each wood component was determined.

From the isothermal heating of oven-dried oak samples in air at 150° and 180° C., Simms and Roberts ( 68 ) obtained an activation energy of 35 kilocalories per mole, using a first-order reaction analysis. A third treatment temperature, 120° C., gave unusable kinetic data, but did seem to cause the formation of some flammable volatiles.

Keylwerth and Christoph ( 41 ) analyzed nine wood species--birch, beech, oak, spruce, pine, larch, poplar, and black locust--using DTA. The results for six of the species are shown in figure 1. The wood samples were ground, sieved (to an unspecified size), and placed in a sintered alumina block for heating. The heat of reaction,  $q_x$ , was calculated from the reaction area,  $F_x$ , in the DTA curve by

$$q_x = \frac{1}{\phi m_x F_x}$$

in which  $m_x$  is the sample mass and  $\phi$  is a calibration factor determined by.

$$\phi = \frac{m_c q_c}{F_c}$$

in which  $m_c$  is the mass;  $q_c$ , the heat of reaction; and  $F_c$ , the reaction area of the calibrating

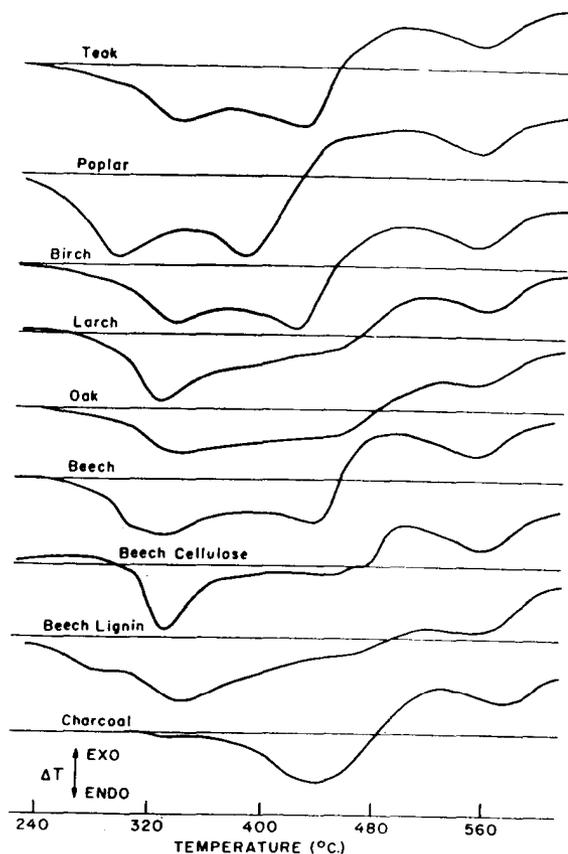


Figure 1.--DTA character sties of six wood species, two components, and charcoal heated in an air atmosphere at 10° C. per minute ( 41 ). (Y-axis scale unspecified. ) M 137 196

materials, benzoic acid and anthracene. A rate of heating of 10° C. per minute was considered optimum for their system. The inert reference material used was not specified.

Beech in an air atmosphere produced a thermogram showing an endotherm between 100° and 220° C. from water evaporation and three exothermic peaks at about 330°, 440°, and 560° C. The reaction was considered complete at about 640° C. No direct correlation of exothermic peaks could be obtained between beech and its constituent components. Thermograms for the wood species exhibited some differences in peak intensities and temperatures, but no marked differences were obtained.

In 1961 Arseneau (4) studied the degradation of powdered balsam fir in air using DTA. The results obtained for various wood fractions and treatments are shown in figure 2. Each sample was powdered by filing, and was sieved to obtain particle sizes between 70 mesh and 200 mesh (75 to 215 micrometers). Calcined alumina was used as a reference material and for sample dilution. Thermograms for extractive free and oven-dry wood were compared with those of air-dry wood for the range from 50° to 420° C., at a heating rate of 5.8° C. per minute. Oven-dry wood lacked some of the peaks present in air-dry wood. Extractive-free wood lacked two endotherms and exotherms noted in air-dry wood. Endotherm at 145° and 163° C. were present in an ethanol-water extract and in the unextracted wood. The benzene-ethanol extract produced an exotherm at 285° C. and in conjunction with lignin at 300° and 360° C. The wood thermogram was concluded to be a composite of the thermograms of individual wood components.

Data collected at the U.S. Forest Products Laboratory and reported by Eickner (21) showed that active pyrolysis began at about 220° C. for ponderosa pine shavings in a dynamic nitrogen atmosphere. Static TGA tests between 300° and 400° C. *in vacuo* gave the results shown in table 1 for both veneer and dowels of ponderosa pine. The reason for the abrupt drop in activation energy for the larger dowels was not known, but is probably related to diffusion phenomena and secondary reactions.

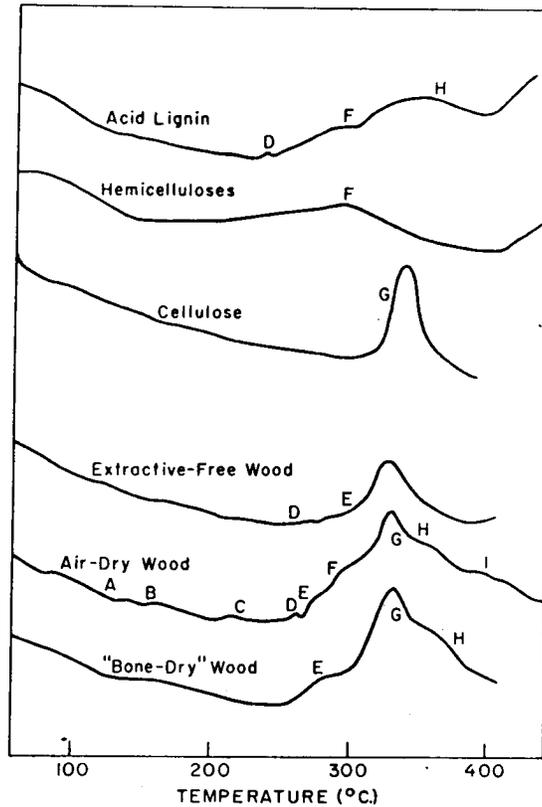


Figure 2. --DTA thermograms of balsam fir and its components heated in air at 5.8° C. per minute (4). Endothermic and exothermic points are identified by letters A through I. M 137 197

Table 1.--Activation energy for untreated ponderosa pine *in vacuo*<sup>1</sup>

Product	Thickness	Activation energy	
		Below 330° C.	Above 330° C.
	Inch	Kcal. per mole	Kcal. per mole
Veneer	0.005	45.6	45.6
	.011	44.9	44.9
	.125	37.8	37.8
Dowels	.250	44.1	44.1
	.375	41.1	28.5
	.500	40.7	28.7

<sup>1</sup>Data from Eickner (21).

Heinrich and Kaesche-Krischer ( 34 ) pyrolyzed oven-dry beech using dynamic TGA *in vacuo* at 1° C. per minute and found changes in the rate of decomposition at 260°, 280°, and 330° C. Subsequent DTA studies, also at 1° C. per minute, indicated that the 260° and 330° C. peaks were exothermic, with the maximum peak at 330° C. DTA exothermic peaks for spruce were found at 280° and 330° C., whereas those for Scotch pine occurred at about 270° and 340° C. While heating in air, a third exothermic peak was observed at a lower temperature-- 210° C. for beech, 190° C. for spruce, and 205° C., for pine. The effects above 220° C. were identical in air and nitrogen because the oxygen in air had been consumed. Activation energies were not determined because of complexities in the TGA curve. The mass for the TGA samples was 20 milligrams, in the form of chips of unspecified size. Thermocouples were placed near the surface and in the center for generation of the DTA curve. DTA samples consisted of wood cylinders of 2.5-centimeter diameter and 3.7-centimeter length. While they were heated at increasing rates from 1° to 12° C. per minute, the TGA thermograms were displaced toward higher temperatures. The residue at 450° C. was 17 percent of the original dry weight in each case.

Domansky and Rendos ( 17 ) pyrolyzed various wood species (spruce, beech, alder, poplar, oak, and white birch) at 10° C. per minute in purified nitrogen, using DTA equipment. The wood was ground to particles of less than 0.3 - millimeter diameter and was oven-dried prior to testing. Thermal degradation of the wood produced three distinct temperature ranges of pyrolysis: Moderately endothermic between 100° and 170° C., exothermic between 210° and 350° C. with a maximum at 270° C., and decomposition above 350° C., without an indicated change. A mixture of wood components of the same composition as natural wood resulted in a thermogram almost identical to that of wood. The variation between wood species was not analyzed, but appeared to have some qualitative significance.

Browne and Tang ( 12 ) investigated the thermal decomposition of ponderosa pine using TGA and DTA. Shavings were used for TGA and ground wood for DTA. The wood was heated at 6° C. per minute for TGA in a 2000 milliliter per minute dynamic nitrogen atmosphere. A comparison was made between untreated samples and fire-

retardant chemically treated wood without a kinetic evaluation. The DTA curves are shown in figure 3.

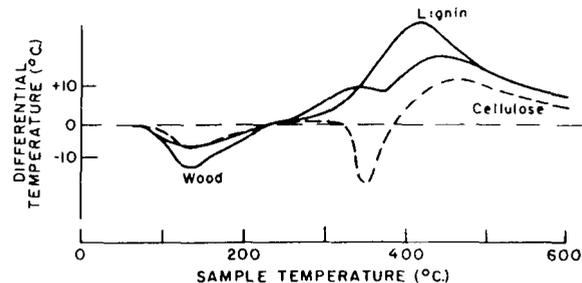


Figure 3. --DTA plot for ponderosa pine, Whatman cellulose, and sulfuric acid lignin heated in nitrogen at 12° C. per minute undiluted with the reference material ( 12 ). M 137 198

A DTA analysis of wood, wood component, and other polysaccharides was made by Sandermann and Augustin ( 62 ) in 1963. Static and dynamic (220 milliliters per minute) air and nitrogen atmospheres were used with a fixed heating rate of 7° C. per minute. Powdered beech and spruce were studied as well as a synthetic wood, composed of the wood constituents in the proper ratio. The results are given in figure 4.

Roberts and Clough ( 60 ) in a first-order reaction interpretation of the pyrolysis of 25-gram cylinders of oven-dry beech by dynamic-static TGA under nitrogen found two values of activation energy--25 kilocalories per mole below about 280° C. and 15 kilocalories per mole above 280° C. The experimental design of the furnace and sample and the high rate of heating (20° C. per minute) caused a lag of about 60° C. of the sample surface and a further 60° C. lag between the center and surface. Exothermic reactions during the static portion of the run were evident from the increased center temperature of up to about 70° C. more than that of the surface.

In the third of a series of studies, Sandermann and Augustin ( 63 ) investigated the decomposition of wood constituents by chemical analysis. Extracted beech sawdust exhibited a small weight loss (3.7 percent) between 206° and 245° C., including pentosan, acetyl, and methoxyl losses. Thermal splitting of lignin was indicated from the large proportion of phenolics obtained by an alcohol extraction. Between 245° and 274° C., hemicellulose decomposition occurred with a

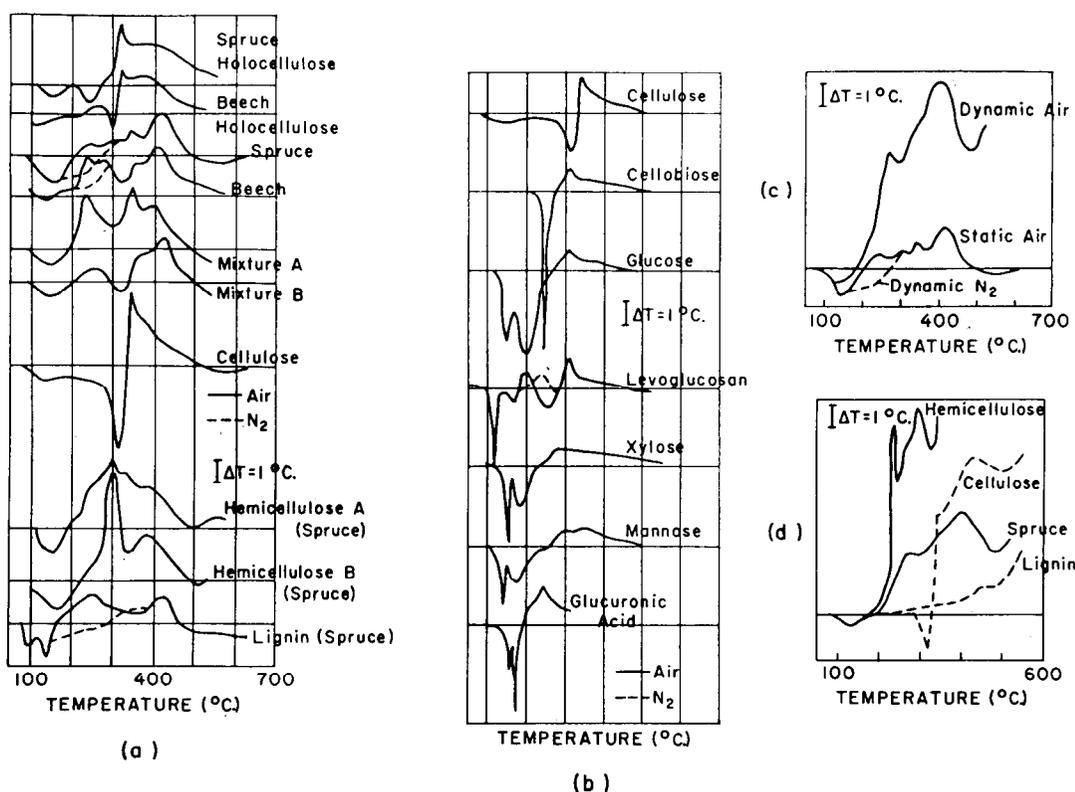


Figure 4. --DTA thermograms of wood, wood components, and various polysaccharides (a through d).

Mixture A: Cellulose, hemicellulose, and lignin in 4:3:3 proportion.

Mixture B: Cellulose and lignin in 4:3 proportion.

Hemicellulose A: 5 percent potassium hydroxide treatment.

Hemicellulose B: 24 percent potassium hydroxide treatment (62).

M 137 195

lignin transformation that appeared to result from a condensation reaction because ethanolysis produced no more derivatives. Between 274° and 329° C., during which the maximum rate of weight loss occurred, the hemicellulose decomposition continued, and cellulose decomposition was evident.

The most comprehensive study to date of the DTA characteristics of wood and wood components is by Domburg and Sergeeva (18). Operational variables considered were the rate and method of heating, quantity and size of material, and the effect of moisture content. The optimum heating rate was found to be 6° C. per minute with an undiluted 1-gram sample. Particle sizes below 50 micrometers produced unusual DTA curves because of the changes unphysical structure caused by grinding. Those above 1000 micrometers transmitted heat unevenly. The

most convenient size was 100 to 200 micrometers. The effects of particle size and moisture content are shown in figure 5. Iskhakov (37), they noted, made the only previous comparable investigation.

Kollmann and Fengel (45) heated oak and pine samples at different temperatures between room temperature and 180° C., and analyzed the loss of the wood components. Pine first lost weight at about 100° C., whereas oak remained stable to about 130° C. It was assumed that the cellulose-hemicellulose interaction in pine caused the reduction of thermal stability between 100° and 130° C.

Piyalkin and Slavyanskii (58) found an increase in activation energy with increasing TGA heating rates for birch. The values were 16.0, 18.3, and 20.6 kilocalories per mole using the Doyle (20) evaluation method for heating rates of 11.4°, 26.6°, and 53.3° C. per minute. The Horowitz and

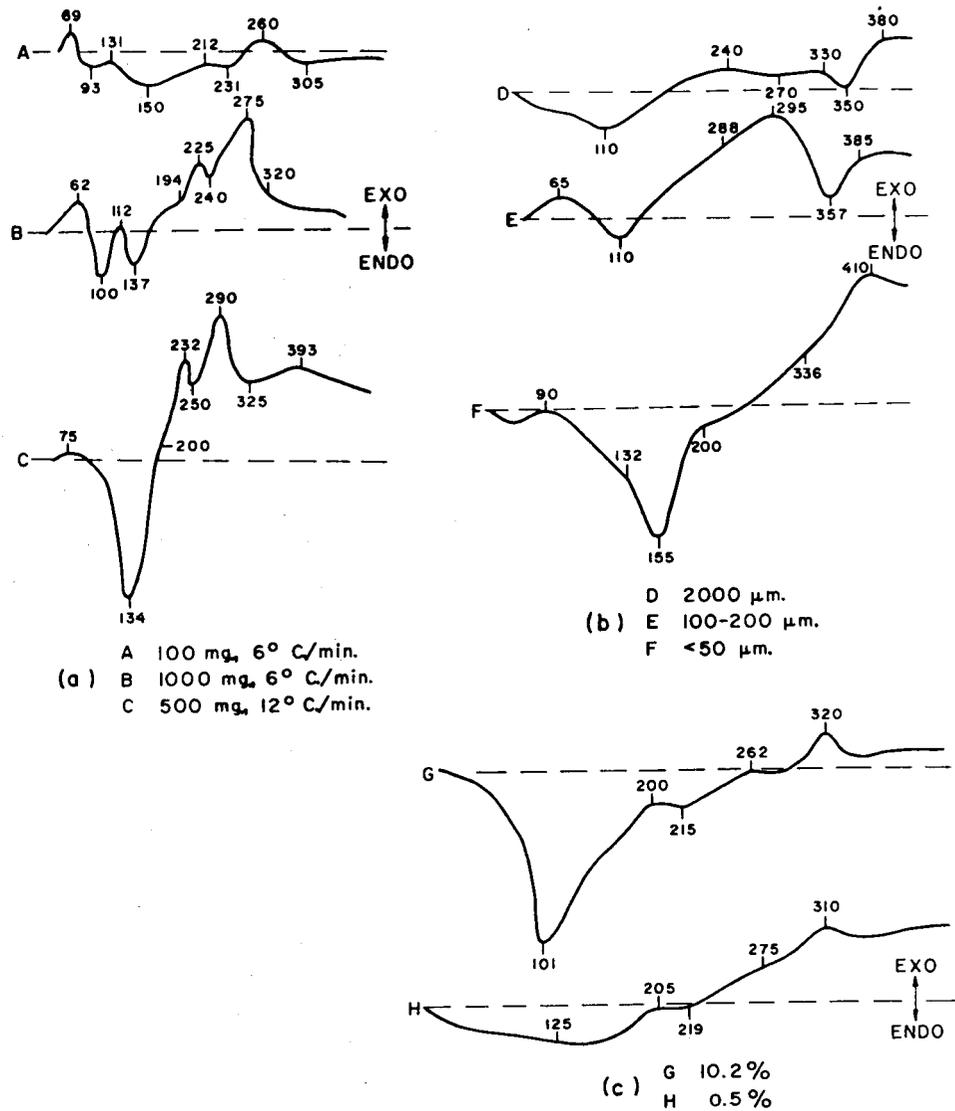


Figure 5. --DTA thermograms of (a) spruce hemicellulose showing the effects of sample size and heating rate, **A**, **B**, and **C**; (b) cellolignin showing the effects of particle size, **D**, **E**, and **F**; and holocellulose showing the effects of moisture content, **G**, and **H**. (18). M 137 199

Metzger (36) evaluation yielded 18.6, 24.6, and 26.0 kilocalories per mole for the same rates. Volatile evolution occurred during two distinct periods, 200° to 250° C. and 250° to 290° C. These two periods merged into one at the higher heating rates. From the curves given, a change in slope occurred at about 50 percent weight loss during the 11.4° and 26.6° C. per minute heating rates. This change in the decomposition rate was not discussed by the authors.

In a recent study, Domburgs et al. (19) conducted a DTA and DTGA analysis of birch and of isolated components such as xylan, cellulose, lignin, cellolignin, and holocellulose (fig 6). The interactions among wood components were used to explain the normal thermogram. The DTGA study was performed with a Hungarian-manufactured thermobalance at 12° C. per minute

using a 100- to 150-milligram sample diluted 2:1 with alumina. DTA was accomplished with an optical pyrometer using 50 to 100 milligrams of sample heated at 6° to 12° C. per minute.

In a TGA study of ponderosa pine degradation, Tang (70) found two activation energy values-- 23 kilocalories per mole between 280° and 325° C. and 54 kilocalories per mole between 325° and 350° C., using first-order kinetics. The wood, in the form of shavings, was heated at 3° C. per minute *in vacuo*. The maximum decomposition rate occurred at 335° C., and the pyrolysis was considered essentially completed at 360° C. with a char residue of 21 percent. Direct use of the Arrhenius equation was made because the Freeman and Carroll method of analysis (26) was considered too unstable. The results are shown in figure 7a, b, and c.

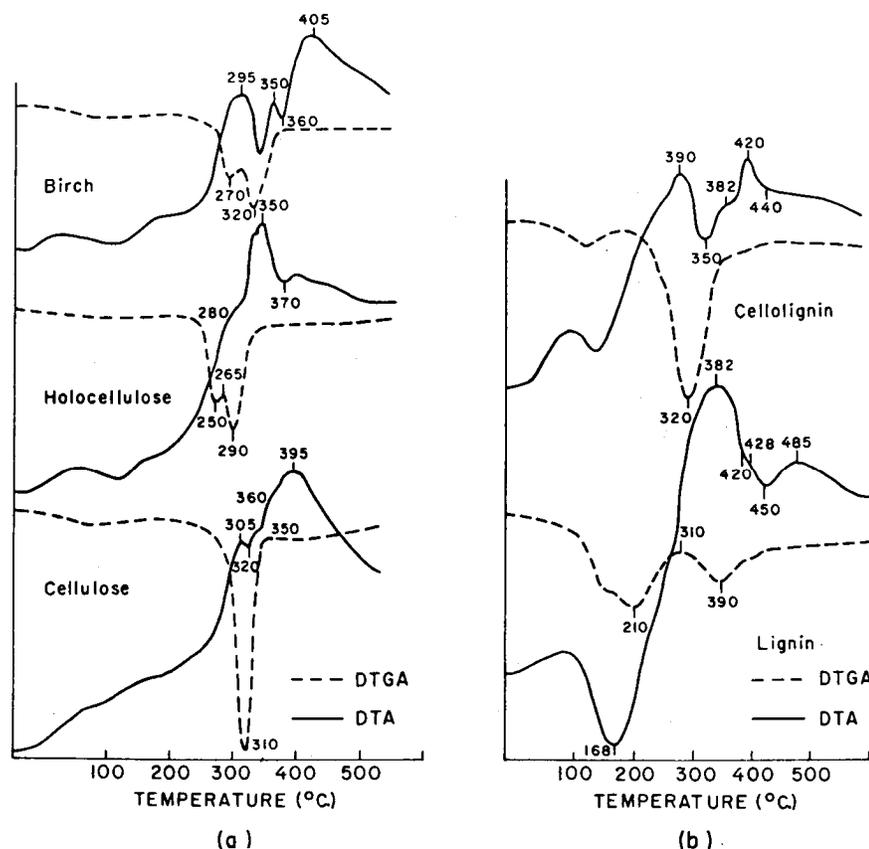


Figure 6. -- DTGA and DTA curves of birch and its components heated at 12° C. per minute in an inert medium (19). M 137 200

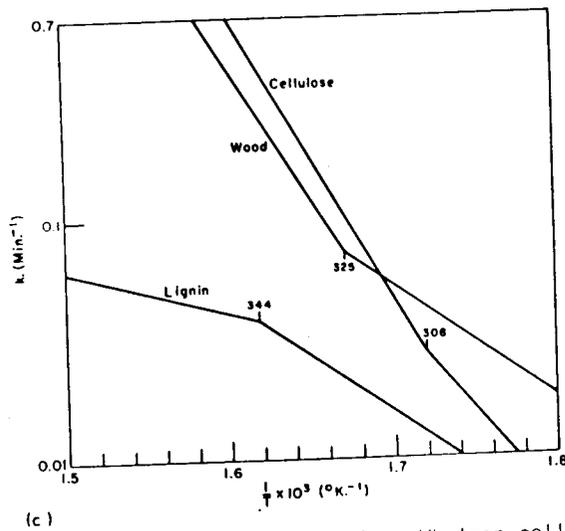
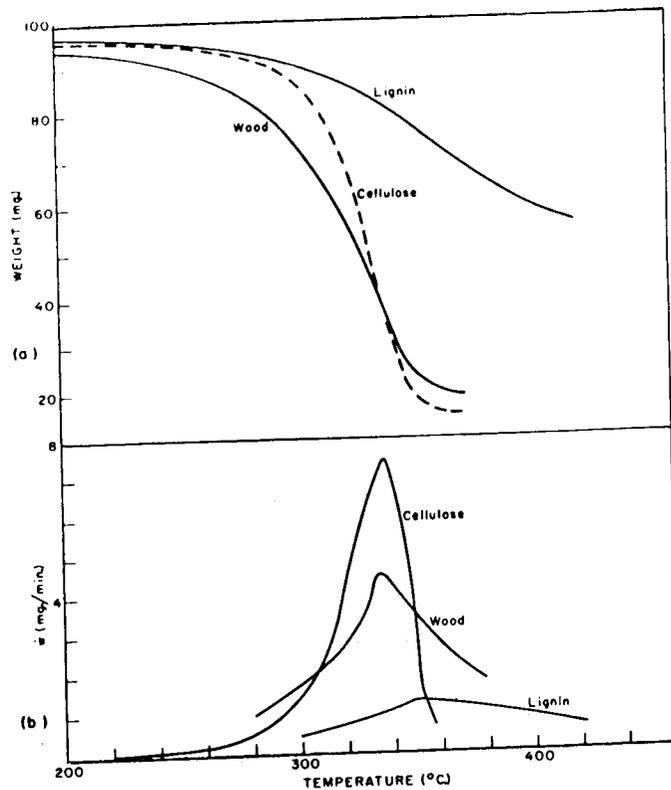


Figure 7.--(a) TGA thermograms of ponderosa pine, Whatman cellulose powder, and sulfuric acid lignin heated at 3° C. per minute in vacuo; (b) Derivative TGA curves obtained from (a) by direct slope measurement; and (c) TGA first-order kinetic plot for ponderosa pine, Whatman powdered cellulose, and sulfuric acid lignin. Slope of lines is equal to the activation energy divided by the gas constant (70).

M 137 201 (a, b)  
M 137 198 (c)

## Thermal Analysis of Cellulose

In investigating thermal decomposition of wood, cellulose has been by far the most frequently studied component. Among the reasons for this are the development of suitable flame or fire retardants or of both, the determination of flash pyrolysis parameters, the relationship between cellulose and wood behavior during pyrolysis and combustion, and the basic mechanisms leading to decomposition and flammability. The reports reviewed in this section are representative of the information available in the literature, particularly the current literature. Less than half of the publications reviewed here are pre-1965, and have been included only if the report added a significant contribution. The reviews are arranged chronologically. The sample characteristics, equipment parameters, and method of data analysis vary considerably among investigators. Although this variance has added some confusion to data analysis, it often indicates the evolution of more refined techniques.

Van Krevelen *et al.* (73) reported an activation energy of about 40 kilocalories per mole for cellulose with the maximum decomposition rate at 315° C.

Sergeeva and Vaivads (67) degraded birch cellulose in air, and measured the DTA thermograms. They interpreted the various endothermic and exothermic peaks and plateaus as follows:

Endotherm 95° to 100° C., evaporation of hygroscopic water.

Plateau: 155° to 259° C., heating of cellulose without bond breaking.

Exotherms: 259° to 389° C. (very steep 299° to 389° C.), to 414° C., and to 452° C.; splitting of cellulose macromolecules.

Plateau: 452° to 500° C., formation of stable substances.

Endotherm 500° to 524° C., completion of reaction.

Stamm (69) found that alpha-cellulose degrades at about the same rate as wood when heated between 110° and 220° C. in an oven. The activation energy under these conditions, assuming a first-order reaction, was 26 kilocalories per mole.

Purified cotton was pyrolyzed isothermally in vacuo for the range from 275° to 305° C. by

Madorsky *et al.* (49). First-order reaction kinetics were applied to the data without considering the initial decomposition, and gave an activation energy of 50 kilocalories per mole. The authors suggest that dehydration takes place randomly along the cellulose chain simultaneously with thermal chain scissions, producing levoglucosan and volatile gases. Levoglucosan is produced only when the glucosan radical forms without the oxygen in the previous ether linkage, and the C-6 hydroxyl group transfers a proton to the C-1 position while forming the 1-6 oxygen bridge. Hydrocellulose, which had a higher crystallinity and a lower degree of polymerization (DP) than cotton, degraded at the same rate ( $E = 47$  kilocalories per mole) and produced the same ratio of products. This implies that chain length and crystallinity have little effect on the direction of pyrolysis.

The theoretical mechanisms of flame retardation are well covered by Gottlieb (32). The effects of flame retardants on cellulose decomposition provide some insight into the adverse conditions that lead to the decomposition of untreated cellulose. The following three well-defined changes occur during the decomposition of flame-retardant-treated cellulose as compared with untreated cellulose: Initial products appear at a lower temperature; initial volatiles are formed at an accelerated rate; and condensable volatiles increase. The increased concentration of initial products is too high for ignition; when diffusion allows the proper mixture with oxygen, these products are too cool for ignition.

Pakhomov (57) has proposed that levoglucosan is formed from an intermediate radical during cellulose degradation. Figure 8 shows the degradation path of cellulose through one of two biradicals to levoglucosan. Radical I transfers a hydroxyl group from C-6 to C-4, whereas Radical II transfers a proton from C-6 to C-4, completing the oxygen bridge C-1 to C-6, forming levoglucosan. The 1-4 glucoside bond appeared the weakest in cellulose because of the high levoglucosan yield.

Golova and Krylova (30) studied the isothermal decomposition of cellulose at 300° C. to determine the molecular changes that occur with treatment time in vacuo. After certain intervals, cellulose was analyzed for, among other things, the degree of polymerization. Two degradation periods apparently occurred. The first caused a

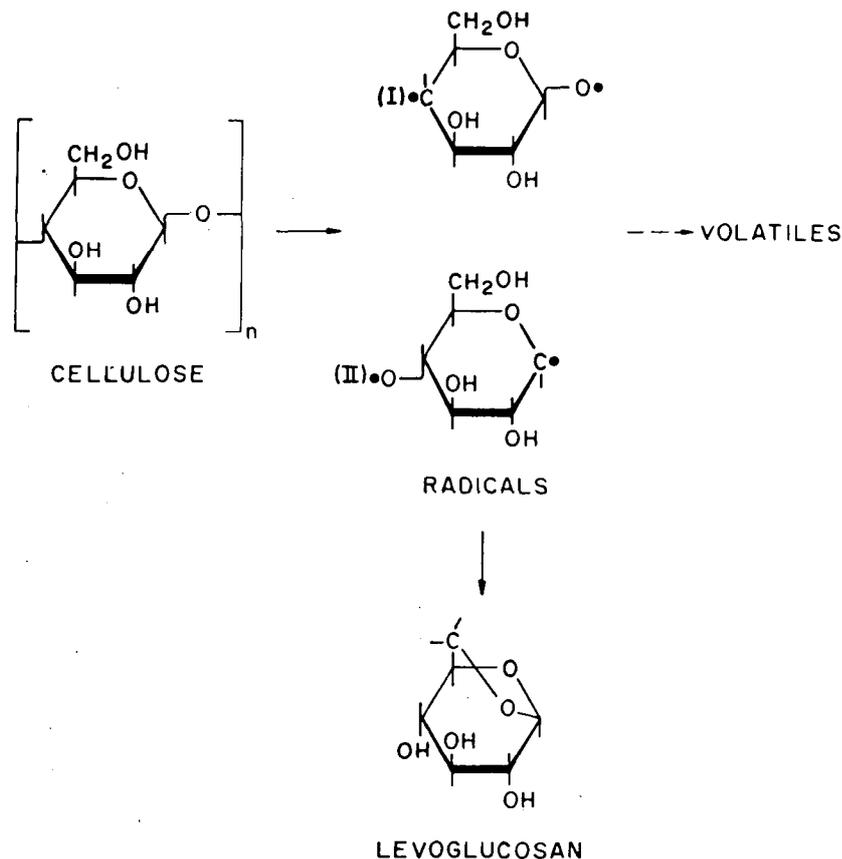


Figure 8.--The proposed decomposition of cellulose via radicals (57). M 137 202

reduction in DP to about 200, during which dehydration was the principal reaction, and the yield of levoglucosan was only about 5 to 20 percent. The second step occurred after the 200-DP level had been attained. During this stage, the levoglucosan yield became constant with time. The 200 DP was maintained during the cellulose decomposition range of 4 to 70 to 80 percent. This study infers that a specific periodicity occurs in the cellulose structure, with a unit of DP 200 representing the next lowest state below the chain macromolecule.

The tars present in aqueous solutions made from untreated cotton fabric pyrolyzed in air at 350° to 375° C. were analyzed by Schwenker and Pacsu (64), and the presence of levoglucosan was quantitatively confirmed. Analysis of the pyrolyzate yielded 12.5 percent levoglucosan, about 15 percent carbonyl compounds, about 7.5 percent acids, and about 55 percent water. The remaining 10 percent was ash.

Schwenker and Pacsu (65) also performed experiments to verify the hypothesis that prevention of the formation of levoglucosan decreases the flammability of cellulose. Although unmodified cotton linters produced 12.5 percent levoglucosan when pyrolyzed in air at 350° C., similar samples, in which about 44 percent of the primary hydroxyl groups were first oxidized to carboxyl groups, produced only 4.9 percent levoglucosan when pyrolyzed. This compared favorably with calculated value of 5.0 to 5.8 percent. Elimination of the C-6 hydroxyl group apparently prevented levoglucosan formation. Furthermore the oxidized cotton burned unevenly, leaving a bulky char without after glow.

Major (51) investigated the isothermal degradation of cellulose (acetate-grade linters pulp) at 170° C.; he concluded that the type of degradation in oxygen was primarily oxidative, whereas that in nitrogen could not be ascertained. Because a DP of about 200 was approached asymptotically

during degradation in oxygen, the oxidation apparently occurred first in the amorphous regions, leaving crystallites unaffected. The value of 200 DP confirmed the observation of Golova and Krylova (30). Although carbonyl groups were formed in both atmospheres, only that of oxygen produced an increase in carboxyl groups. Some carbonyl groups must have formed along the cellulose chain because the number of end groups could not alone account for the high measured concentration. In the nitrogen atmosphere, the concentration of carbonyl groups reached a constant level after an initial rapid increase. This effect was unexplained, but it was speculated that the initial increase was caused by oxygen impurities in the prepurified nitrogen. Prior literature on the thermal degradation of cellulose was also well covered in this paper by Major.

In pyrolyzing various derivatives of cellulose, Mardorsky *et al.* (50) found that oxidation of the primary alcohol to an acid not only introduces a steric hindrance to the formation of levoglucosan, but also weakens the cellulose ring to a degree that it pyrolyzes at low temperatures. If, however, the alcohol is first esterified, tar formation is reduced and thermal stability is maintained.

According to Holmes and Shaw (35), when cotton is heated in dry air instead of *in vacuo*, both oxidation of the products and secondary reactions occur, thus reducing the tar fraction. X-ray analysis of poplin char residue from isothermal *in vacuo* pyrolysis of cotton at 418° C. revealed that no crystalline structure was retained by the cellulose. When impurities were removed from cotton samples, more tar was formed during pyrolysis.

In a DTA study, cellulose from four different sources were tested in nitrogen by Domansky and Rendos (17) -- Whatman paper, spruce sulfite cellulose, spruce sulfate cellulose, and beech sulfate cellulose. The exothermic reaction began at about 230° C. for all four samples and became endothermic at 315° to 320° C. Of the four, only the Whatman paper sample, which showed a 5° C. delay in reaction peaks, exhibited a significant variation.

Murphy (55) determined the rate of evolution of gases from cellulose *in vacuo* for the temperature range of 100° to 250° C. Two activation energies characterized the gas evolution, an initial energy of 34.0 kilocalories per mole and a final of 39.4 kilocalories per mole. The initial

activation energy was attributed to the degradation of chain ends and secondary substances, producing a gas ratio of  $3\text{H}_2\text{O}:1\text{CO}_2:1\text{CO}$ . The

second activation energy was associated with cellulose depolymerization and degradation, producing a gas ratio of  $10\text{H}_2\text{O}:2.5\text{CO}_2:1\text{CO}$ . Kraft

paper (5 percent lignin, 5 percent hemicellulose) and linen (99 percent cellulose) exhibited the same activation energies in both stages of decomposition. No induction period or autocatalytic reaction occurred.

Tang and Neill (72) performed TGA and DTA experiments on cellulose paper and powder; each contained a minimum of 99.3 percent cellulose. In the TGA study, the samples were heated at 3° C. per minute *in vacuo*, using 100-milligram samples. Active pyrolysis began at 270° C. and produced a 14-milligram char. Two stages of decomposition were evident, the first between 240° and 310° C. with activation energies of 33.1 to 35.2 kilocalories per mole, and the second between 310° and 360° C., with energies of 53.1 to 55.7 kilocalories per mole. The kinetic order of the first stage was zero, whereas that of the second stage was first order.

DTA runs were made with helium or oxygen at 30 milliliters per minute flow rate, whereas the sample, mixed with pyrex beads (about 30 micrometer diameter), was heated at a nominal 12° C. per minute. During pyrolysis in helium, an endothermic peak occurred at 335° C., the temperature corresponding to maximum rate of weight loss. The reaction was essentially complete at 360° C. During combustion in oxygen, an exothermic peak was observed at 335° C., and slowly diminished. Glowing occurred until about 460° C., the point at which the sample was totally consumed. A value of  $88 \pm 4$  calories per gram was obtained for the heat of pyrolysis of cellulose, using the peak area from DTA, and calibrating the apparatus with benzoic acid, silver nitrate, and potassium nitrate. The heat of combustion calculated from DTA data was found to be 3540 calories per gram excluding the initial pyrolyzed products. Oxygen-bomb calorimetry produced a value of 4030 calories per gram about 12 percent higher than that of DTA. Keylwerth and Christoph (41) had previously obtained 3.1 kilocalories per gram for the heat of combustion of beech cellulose using DTA.

The effect of thermal treatments on the fine

structure of cellulose was investigated by Millett and Goedken (52). Cotton linters were heated isothermally at temperatures between 180° C. and 260° C. for 0 to 64 hours. An apparent first-order reaction occurred for this range giving an activation energy of 31 kilocalories per mole.

The degree of polymerization of slash pine sulfite pulp was found to decrease threefold for each 20° C. increase of temperature. Half-life values were the following: 180° C., 4.5 hours; 200° C., 1.5 hours; and 240° C., 0.3 hour.

Arseneau (4) used an unconventional method in a DTA study of cellulose. Because alumina acts as a catalyst for certain cellulose reactions, the "sample cell was filled to the thermocouple junction, without covering it, and the reference cell was left empty. By this method, the radiant heating of the thermocouples was similar, and sharp reaction peaks were obtained with good baselines. A 5-milligram sample of Whatman No. 1 filter paper was heated at about 8° C. per minute in an air atmosphere. Activation energies calculated from the DTA peaks, using Kissinger's method (43) were 27.8 and 34.5 kilocalories per mole for the first and second peaks, respectively, for a temperature range from ambient to about 450° C. These two peaks were interpreted as representing the decomposition of surface impurities, or chain ends, followed by the breakdown of crystalline areas, as proposed by Murphy (55). Although Kissinger's method requires several heating rates, these were not specified, nor were the purity and rate of flow of air. From his DTA block diagram it appears that the decomposition was carried out in a self-generated atmosphere. Arseneau (5) and Tang and Eickner (71) have used DTA analysis to study the influence of chemical treatment and of cellulose on its thermal degradation.

The mechanism of cellulose decomposition has been studied by Kilzer and Broido (42) who proposed the following reactions:

1. Dehydration of cellulose to "dehydrocellulose" between about 200° and 280° C.
2. Depolymerization of cellulose in competition with dehydration between 280° and 340° C., resulting in the formation of volatiles.
3. Decomposition of dehydrocellulose into gases and char residue via an exothermic reaction that becomes dominant at about 320° C.

The volatiles formed during depolymerization are classified as tars, and consist primarily of

levoglucosan. It was hypothesized that inorganic impurities catalyze dehydration and, consequently, there is decomposition into gases and char. This reduces the effect of the competing depolymerization reactions through which tar formation occurs. The decomposition gases are primarily water, carbon dioxide, and carbon monoxide.

The mechanism of dehydration is said to be the only possible reaction between adjoining cellulose chains because none of the intra- and inter-ring and intra-molecular reactions meet the energy requirements. This dehydration reaction occurs from etherification of the C-6 hydroxyl with the C-4 position of the adjoining chain. The acetal form of the carbonyl group then rearranges to a free aldehyde. The intermediate aldehyde end group may collapse to yield water and a tetrahydro-5-hydroxymethylfurfural end group. This overall reaction mechanism prevents unzipping of the reacting cellulose molecules, and makes the ether-linked chains difficult to volatilize. The decomposition of dehydrocellulose to gases and water is rather easily explained. It is proposed that depolymerization produces levoglucosan by the following mechanism:

1. Scission of the two monomer glucoside bonds or of a single bond for the terminal group and rearward attack of the oxygen between the C-1 and C-4 positions. This causes a transition to the boat conformation and formation of 1,4-anhydro- $\alpha$ -D-glucopyranose.

2. Internal rearrangement resulting from attack of the C-6 hydroxyl group on the C-1 position, breaking the 1-4 ether bridge, and forming a 1-6 bridge, thus producing 1,6-anhydro- $\beta$ -D-glucopyranose (levoglucosan). Alternately, but less favorably, the scission of the 1-5 bridge could lead to 1,6-anhydro- $\beta$ -D-glucofuranose, a minor pyrolysis product. The unzipping reaction could occur readily by these decomposition modes.

According to Domburge *et al.* (19), cellolignin (wood having only the hemicelluloses extracted) will produce levoglucosan only if a certain physical structure is maintained. Cellolignin that was degraded in a vibro-mill did not form levoglucosan, and produced a different thermogram than did the untreated sample.

Bryce and Greenwood (13) compared the thermal decomposition of cellulose with that of its  $\alpha$ -anomer, amylose, in a study of starch degrada-

tion. The relative thermal stability was measured by the amount of pyrolytic residue. The rate of evolution of volatiles *in vacuo* was determined for the range from 156° to 337° C. A 50-milligram sample of finely divided Whatman No. 1 chromatography paper was predried before the isothermal pyrolysis. From the shape of the H<sub>2</sub>O-CO<sub>2</sub>-CO

curves vs. time, it was concluded that no induction period or autocatalytic process was involved. This confirmed Murphy's (55) observations. The production of carbon dioxide was in two first-order reactions; the first, a rapid reaction, followed by a slower second one. Comparable results were found for carbon monoxide. In a plot of carbon dioxide and of carbon monoxide generation vs. water yield for a wide range of temperatures, a linear relationship was found above a certain threshold level of water. The limiting production rates for the H<sub>2</sub>O: CO<sub>2</sub>: CO ratio was 16:5:1 for cellulose. The ratio appeared to be related to thermal stability. The activation energy, based on initial carbon monoxide and carbon dioxide generation rates, was 29 kilocalories per mole for cellulose.

Three stages were noted by Lipska and Parker (48) in an isothermal study of the pyrolysis of alpha-cellulose between 250° and 300° C.:

1. A temperature-dependent stage, characterized by rapid decomposition and weight loss, amounting to 2 percent at 250° C. and 6.5 percent at 298° C. This stage could not be explained on the basis of oxidation from impurities in the prepurified nitrogen, from reactions with trapped oxygen, or from the loss of moisture. According to the authors, this rapid decomposition does not occur during the pyrolysis of cotton cellulose. The authors gave no explanation, but it would seem that the different behavior stems from the residual noncellulosic carbohydrate esters that are present in alpha-cellulose.

2. A zero-order stage for both decomposition and volatilization, which for the 288° C. sample, occurred between 6 and 50 percent volatilization.

3. A final first-order stage leaving a pyrolysis residue of about 16 percent for the samples at temperatures between 275° and 300° C.

Decomposition was determined by a glucose analysis of the pyrolyzed sample, whereas volatilization was measured by the weight loss. The activation energy for both decomposition and volatilization was 42 kilocalories per mole for

the 250° to 300° C. range of the zero-order stage. The 250° C. sample data appeared to fit a first-order reaction for the entire decomposition range.

Broido (10) compared ashfree cellulose (less than 0.01 percent ash) and pure cellulose (0.15 percent ash) by DTA and TGA in both nitrogen and air atmospheres. The 500-milligram paper samples were suspended by a Nichrome wire and heated at a nominal 6° C. per minute in an Aminco Thermograv. In nitrogen, the ashfree cellulose began losing weight at about 285° C., with most of the weight loss occurring within the next 100° C. At higher temperatures, the sample approached a 10 percent residual char. The pure cellulose sample began degrading at about 260° C. at a much slower initial decomposition rate than the ashfree material. The reaction terminated at about the same temperature, however, but left a greater residual char of about 15 percent. The initial endotherms for each sample between 100° and 200° C. were attributable to the loss of water. Each sample underwent a change between 200° and 250° C. that may be interpreted as indicating competing processes. Characteristic endothermic reactions appeared at about 300° C. and exothermic at about 350° C., and were much better defined for the sample containing less ash. In a static air atmosphere, the TGA curves were similar in shape to the nitrogen atmosphere curves, although the initial weight loss for each material occurred at a slightly lower temperature. The DTA curves, by contrast, reflected the complexity introduced by the presence of oxygen in the air.

Byrne, *et al.* (14) support the view of Madorsky *et al.* (49) that 1,2-anhydro- $\alpha$ -D-glucopyranose is an intermediate in the formation of levoglucosan. Figure 9 shows the possible sequences leading to levoglucosan. It was hypothesized that the rate of formation of levoglucosan is regulated by the configurate ion of the glucose unit--whether it is in the chair or boat form.

Observations of the quantitative yield of furfural from cellulose and levoglucosan decomposition in air at 350° C. led Kato *et al.* (39) to suggest that cellulose is not always decomposed via levoglucosan.

Using X-rays for measurement of mass loss and transfer, Murty and Blackshear (56) studied the pyrolysis and combustion of alpha-cellulose cylinders. Temperature profiles were obtained by use of thermocouples implanted at various radii

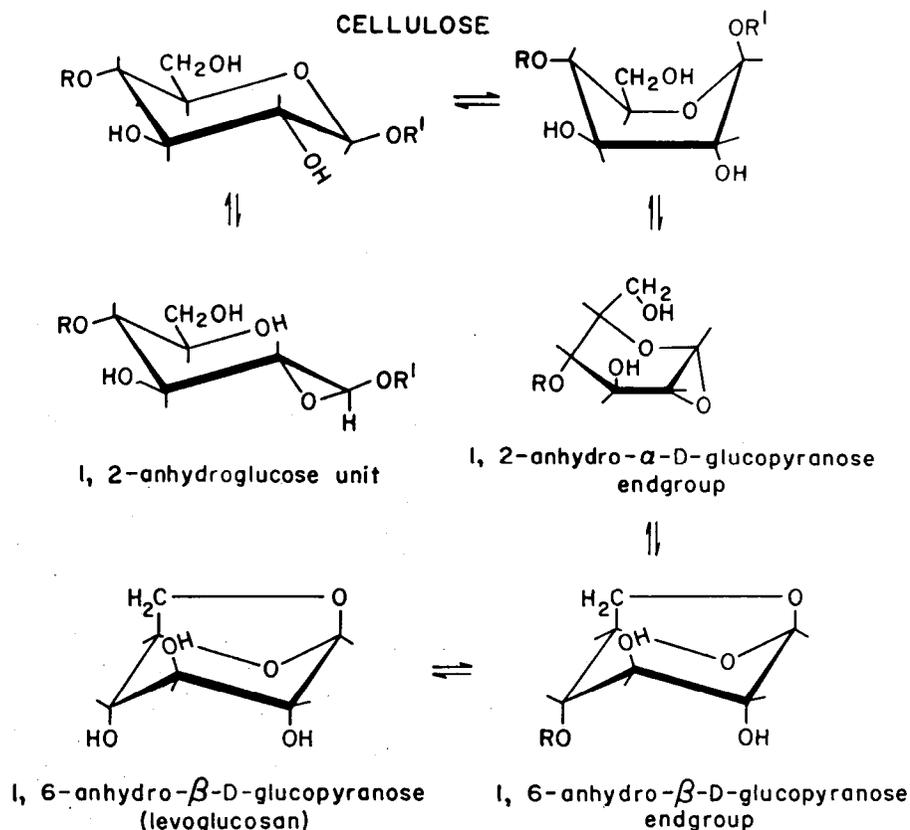


Figure 9.--The proposed decomposition of cellulose via intermediate configurations (14).

M 137 203

within the cylinders. Endotherm were noticeable at 125° and 375° C., whereas beyond about 400° C., the reaction was exothermic. They speculated that volatiles formed at the surface of a solid (of sufficient thickness to have an appreciable temperature gradient) diffuse toward the internal cooler part where they condense. When subsequent evaporation occurs as temperatures in this region increase, a second endothermic reaction occurs. Measurement of the mass loss with time was used to compute first-order activation energies, which range from 13 to 22 kilocalories per mole, depending on the depth of pyrolytic penetration. The interiors of the cylinders produced lower activation energy values than the surface layers, presumably because of the longer exposure to high temperatures and also because of the effect of the migrating volatiles. If alteration in the cellulose structure occurred because of these factors, the decomposition could have conceivably progressed more rapidly. The structural alteration was assumed

to lead to the formation of dehydrocellulose. Within the range of radii-dependent temperatures, centered around 300° C., the reaction appeared to be independent of temperature. This is due presumably to evaporation of the condensed volatiles. Activation energies appeared to be directly temperature dependent, although the data were somewhat scattered. Murty and BlackShear stressed that the apparent kinetic constants were highly dependent on specimen size, composition, and heating rate.

A recent investigation of the kinetics of cellulose pyrolysis was made by Chatterjee and Conrad (15) for the range from 270° to 310° C., using absorbent cotton and ball-milled scoured cotton. The ball-milled cotton was amorphous, whereas the absorbent cotton was not and had a DP of 1925. A dynamic (170 milliliters per minute) helium atmosphere was used to remove volatiles. The 100-milligram samples were heated at 3° C. per minute to the isothermal temperature for pyrolysis.

Decomposition apparently began between 260° and 265° C. at the lower temperature range of study. The effective end-temperature of decomposition was 350° C. Pyrolysis appeared to be a two-step reaction, the first with no simple reaction order, whereas the second appeared to follow first-order kinetics. The reactions were considered to consist of the initiation and propagation mechanisms of polymer decomposition, with the formation of only one intermediate volatile, levoglucosan. Absorbent cotton yielded activation energies for the initiation and propagation steps of 54.3 and 33.0 kilocalories per mole, whereas ball-milled cotton yielded energies of 75.0 and 37.1 kilocalories per mole.

The first 40 percent decomposition did not follow any simple order of reaction. Beyond this, the data fitted a first-order reaction, and the propagation activation energy was determined from the weight-loss vs. time data, using the Arrhenius equation. The initiation activation energy was determined by subtracting the apparent propagation energy value from the derived sum of the activation energies. The values obtained for the initiation activation energy do not agree with values reported in the literature and are derived directly from, the propagation value. Also, the derived kinetics apply only if the unzipping starts at the end of a chain rather than elsewhere and if levoglucosan is formed as an intermediate.

Lipska (47) has reviewed the processes of oxidation and pyrolysis for cellulosic materials. Her review also covers methods of measurement, the potential of toxic hazards from product gases,

and the effects of fire retardants. The report concludes with a number of recommendations, including one for more intensive study in the region between 300° and 400° C. in which most of the volatiles are produced.

Akita and Kase (2) used Kissinger's method (43) to evaluate the pyrolysis of ashfree cellulose filter paper by simultaneous TGA-DTA measurements. The sample was powdered and diluted with aluminum oxide, and heated at 5° C. per minute. Preliminary tests indicated that the reaction was first order ( $1.054 \pm 0.065$ ) and that the activation energy was constant ( $53.51 \pm 0.94$ ) for the heating rate range of 0.23 to 2.40° C. per minute and temperature range of about 280° to 320° C.

Kato and Takahashi (40) studied the isothermal degradation of microcrystalline (DP = 200) cellulose in dynamic nitrogen and air atmospheres between 240° and 300° C. Because the weight vs. time curves were linear during the rapid decomposition, the log of the slope was plotted vs. 1/T to determine the activation energies. These are listed in table 2 with values obtained for cellobiose and glucose. The authors used zero-order kinetics to evaluate the activation energies although they did not state this. No attempt was made to evaluate any other portions of the degradation curves. An increase in the concentration of carboxyl groups was noted in both nitrogen and air atmospheres. Oxidation of cellulose in the nitrogen atmosphere was said to have occurred from glucosidic and pyranose bond scissions. In air, however, the concentration of carboxyl groups

Table 2.--Activation energies for the rapid degradation stage of microcrystalline cellulose, cellobiose, and glucose obtained from zero order kinetics<sup>1</sup>

Sample	Atmosphere	Temperature range	Activation energy
		°C.	Kcal. per mole
Cellulose	Air	240-300	16.9
	Nitrogen	240-300	22.0
Cellobiose	Air	240-300	18.3
	Nitrogen	230-290	16.9
Glucose	Air	220-280	17.8
	Nitrogen	230-290	18.8

<sup>1</sup>Data from Kato and Takahashi (40).

increased over that observed in nitrogen, apparently because of the free oxygen.

Kato (36) studied the pyrolysis of cellulose and of cellulose constituents in helium to determine the direction of pyrolysis. On the basis of a previous study and from the proposal of Pakhomov (57), it was postulated that the volatilization of cellulose occurs through the presence of intermediate free radicals that under the proper conditions can form levoglucosan (fig. 8). Data obtained indicated that two simultaneous primary reactions occur: The initial scission of glucosidic bonds and chemical changes in cellulose anhydroglucose units before glucosidic bond breaking. The levoglucosan mechanism of degradation was not supported as the result of a study of the formation of furfural and furan from cellulose and from levoglucosan.

Tang (70) found that the degradation of cellulose (Whatman No. 1 chromatography paper) followed a first-order reaction (fig. 7c) with two activation energies: 35 kilocalories per mole between 240° and 308° C. and 56 kilocalories per mole between 308° and 360° C. The work was carried out *in vacuo* using a heating rate of 3° C. per minute.

In a study of the carbonization of polymers during pyrolysis, Dollimore and Heal (16) found that Whatman ashless filter paper is nonfusing and nongraphitizing. In a DTA study, cellulose exhibited endotherm at 115° and 359° C. and an exotherm at 326° C. A tentative conclusion reached is that an exothermic reaction in the first stage of decomposition indicates that the final product will be a nongraphitic carbon.

Fengel (25), in the last of a four-part study on thermally induced changes in wood at temperatures up to 200° C., investigated the effects of thermal treatment in spruce cellulose between 20° and 200° C. Because of the loss of water between chains, cellulose became more acid-resistant near 100° C. An accompanying increase occurred in the number of bonds that could be easily split in the alkali-resistant cellulose. An apparent decrease in the amount of alpha-cellulose up to 120° C. was attributed to residual lignin obtained from the extraction process. From 120° to 180° C., the mannan content was partially responsible for the alpha-cellulose loss. After a 200° C. treatment, only traces of noncellulosic materials were present in the alpha-cellulose. The most crystalline portions of cellulose were the most stable thermally and the most resistant to hydrolysis.

Ramiah and Goring (59) used a sensitive method, based on gas evolution, to determine initial decomposition temperatures of different forms of cellulose, and computed the first-order activation energy. The decomposition began at about 164° C. and gave a range of activation energies from about 123 to 155 kilocalories per mole. Cellulose was considered the most stable wood constituent.

#### Thermal Analysis of Hemicelluloses

The hemicelluloses are among the wood components least investigated. This group of carbohydrates has been included in survey studies, but virtually no comparisons have been made between the types of hemicellulose. Most studies have been made using DTA, and the TGA data available are of little qualitative or quantitative value.

Sergeeva and Vaivads (67) investigated the DTA characteristics of xylan isolated from birch. They noted that hydroscopic water is more difficult to remove from xylan than from cellulose; this reflected in the deeper and more prolonged endotherm of the xylan. A plateau between 175° and 210° C. precedes the primary exothermic reaction. The decomposition is completed by 273° C., and is followed by a heating of the residual mass between 273° and 330° C. After this a deep endotherm occurs that is attributed to secondary reactions leading to the formation of gases. A total of four endotherm and three exotherms was noted by the authors. However, the procedure, equipment, and sample pretreatment were not sufficiently controlled to produce a reliable curve.

Kudo and Yoshida (46) carbonized wood samples by dry distillation and analyzed the samples at various temperatures between 150° and 500° C. for ether extract, 1 percent NaOH extract, and reducing-sugar yield, as well as other factors. A nominal heating rate of 0.3° C. per minute was used. Both natural extractives and hemicelluloses decomposed between 150° and 200° C., with a hemicellulose decomposition limit at about 280° C.

Some of the early literature reviewed by Browne (11) had proposed that hemicelluloses were a major source of acetic acid. Minami and Kawamura (53), however, found that just about as much yield of acetic acid was obtainable from the destructive distillation of cellulose. The

observed decomposition of hemicelluloses extracted from *Quercus glauca* was said to be similar to that of hemicelluloses in the untreated wood.

Arseneau (4) analyzed the hemicellulose portion of balsam fir by DTA and obtained the curve shown in figure 2. An exothermic peak was gradually attained at 285° C., but this was considered the combined exotherms of the benzene-alcohol extract and of the acid lignin at 290° C.

Hemicelluloses isolated from four woods, beech, spruce, poplar, and maple, were analyzed by Domansky and Rendos (17) while heated in a nitrogen atmosphere in a DTA study, with the results shown in figure 10a. The initial endotherm represents a bound-water loss. An exotherm, beginning at about 180° C., extends through the peak at 255° C. Beyond 300° C., some exothermic behavior is evident, but to a lesser degree. From these thermograms, the authors concluded that the hemicelluloses were the least thermally stable constituents in wood. They hypothesized that the relatively unstable condition of the hemicelluloses at temperatures below those at which cellulose decomposes is a result of their amorphous nature.

From isothermal studies of oak and pine decomposition, Kollmann and Fengel (45) concluded that cellulose stability is reduced because of interaction with hemicelluloses. The hemicellulose content remained constant between 150° and 180° C., even though the pentosan content decreased. This discrepancy is explained by an increase in hexosan content resulting from fragmentation of the cellulose. Treatment time had little effect on the amount of hemicellulose decomposition.

Fengel (22) heated spruce in air to various temperatures and then performed hot- and cold-water extractions to determine the thermal effects on the hemicelluloses. The quantity of hot-water extract increased for wood heated above 100° C., whereas that of the cold water increased above 120° C., with the largest increase in both extracts occurring between 150° and 180° C. The amount of xylan increased in the cold-water extract up to 180° C., whereas the arabinose content decreased beyond 120° C. It was proposed that hemicellulose decomposition follows two stages: (1) A partial decomposition of the macromolecules into fragments that are water soluble, and, (2) either a depolymerization of short chains to monomer units and subsequent decomposition to volatiles or a rapid direct decomposition of the

polymer chain to volatiles at such a high rate that detection of fragments is difficult.

A subsequent study of hemicellulose behavior during heating was made by Fengel (23). Milled spruce that was isothermally treated at temperatures between 80° and 200° C. was extracted with 5 percent and 24 percent potassium hydroxide solutions to remove alkali-soluble hemicelluloses. Six fractions, of which five were polysaccharides, were separated from the hemicelluloses. Fraction B1 (0.6 percent of the untreated, extractivefree wood) was a galactoglucomannan having a fibrillar nature. Fraction A1 (0.1 percent of the untreated, extractivefree wood) was thought to contain glucan-forming globular particles with a lamellar structure. The three remaining polymer fractions (B2, A2, and A3) were composed of mannose and xylan residues. Fraction A3 contained film-forming granular particles, whereas B2 and A2 showed a fine fibrillar amorphous structure. Up to 180° C., fraction B1 increased to about 9 percent and showed a glucose increase in the hydrolysate. The quantity of hemicellulose B increased, probably because of extractable cellulose fragments. A decrease in hemicellulose A coincided with a pentosan decrease, in fraction A3, the smallest of the alkali-soluble substances and probably the first to decompose. Between 180° and 200° C., the quantity of hemicellulose A increased, which, with hemicellulose B at lower temperatures, probably resulted from cellulose fragments.

Xylan separated from wood degrades differently, depending on whether an inert medium or vacuum is used, according to Domburgs *et al.* (19). Figure 10b shows that xylan under normal pressure begins decomposing near 200° C. with an endotherm peaking at 220° C. Along with C-O-C bond rupture, some pyranose C-C bonds also are broken. Thermal pretreatment at 225° C. was found to completely obliterate the polysaccharide structure. Above 225° C., a rapid exothermal process, which peaks between 275° and 290° C., occurs from fragmentation and gas evolution. The molecular fragments are dehydrated, producing furfural. Beyond 300° C., further secondary reactions take place, resulting in a graphitic structure. Under vacuum, furfural production is apparently prevented because of cross-linking. Rapid decomposition occurred from about 220° C. with C-O-C bonds ruptured and forming anhydride compounds. The deep endotherm between 250° and 300° C. resulted

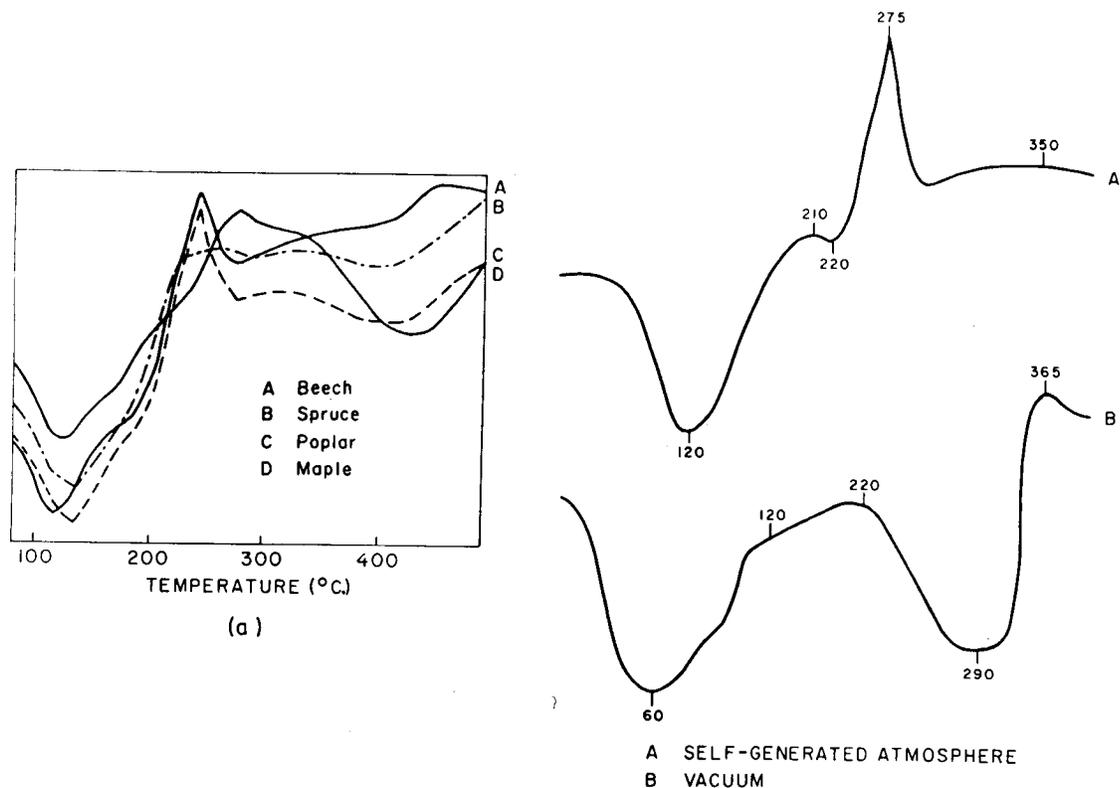


Figure 10. -- (a) DTA thermograms of hemicelluloses isolated from beech, spruce, poplar, and maple in a nitrogen atmosphere (17); (b) degradation of hardwood xylan under atmospheric pressure (upper curve) and in vacuo (lower curve) (19). M 137 204

from evaporation of the anhydrides. Degeneration of chain fragments then occurred at a higher temperature.

In an investigation of the thermal degradation of isolated wood components using the gas evolution method, Ramiah and Goring (59) found that birch xylan began degrading at 117° C. with an activation energy of 46 kilocalories per mole. Pine glucomannan began degradation at 127° C. and was presumably more stable because of its partial crystallinity. The first-order activation energy for decomposition was 50 kilocalories per mole. It was concluded that the hemicelluloses were the least stable of the wood components.

#### Thermal Analysis of Lignin

Little information is available on the TGA and

DTA characteristics of lignin. Most of the literature reviewed on the thermal properties of lignin is superficial, and contributes little toward increasing the basic knowledge of the interaction of lignin and the polysaccharides in wood.

Breger and Whitehead (9) conducted an in vacuo DTA analysis of various types of lignin. The curves in figure 11a show the differences in thermal reactions of different lignin types. Two exothermic peaks are evident, the first at 400° to 440° C., and the second at about 675° C. The shoulder at about 380° C. for periodate lignin was said to be caused by residual cellulose. The Russell synthetic lignin appears to have properties similar to those of the isolated lignins.

Van Krevelen et al. (73) have reported the activation energy for the decomposition of lignin (method of preparation not reported) as 28 kilocalories per mole with the maximum rate at 354° C.

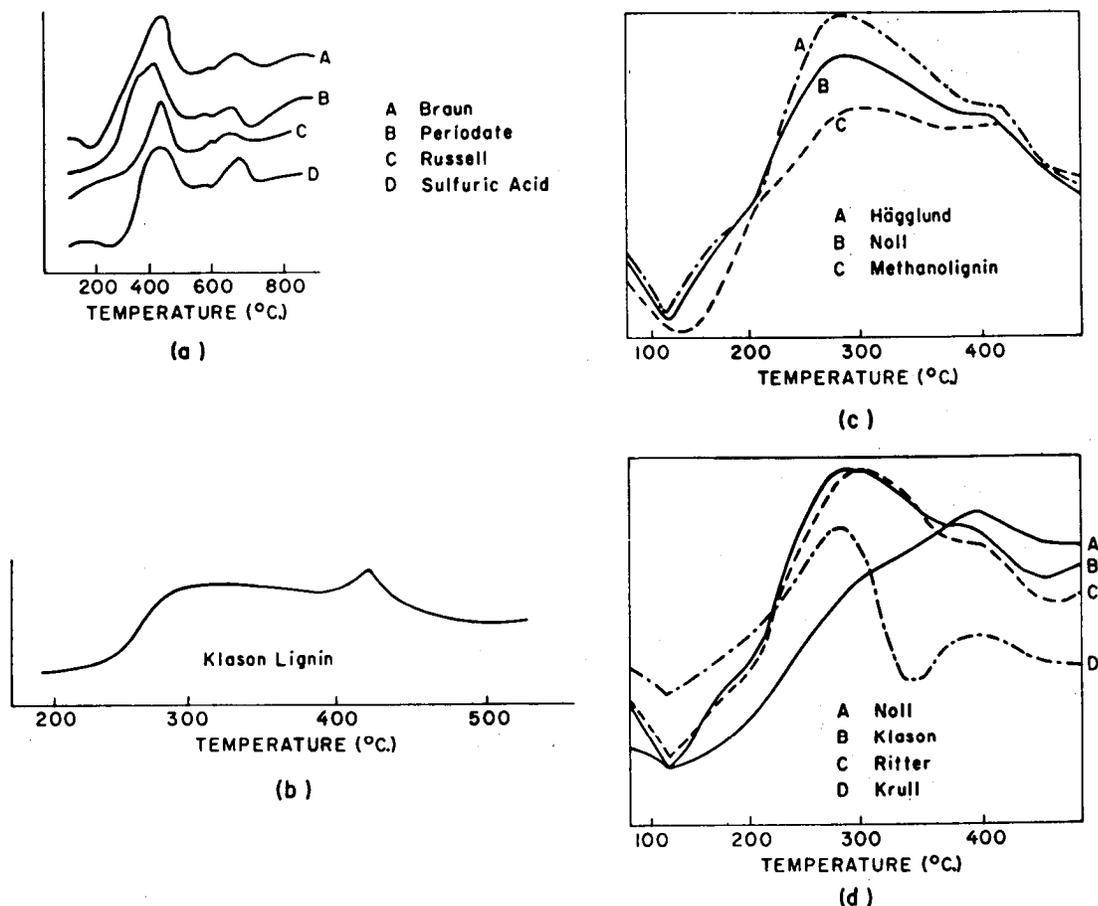


Figure 11. --DTA variation of different lignin preparations; (a) *in vacuo*, and (b), (c), and (d) in inert atmospheres.

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Stamm (69) determined that at 150° C., lignin degrades at about one-half the rate of wood. The activation energy for lignin degradation in an oven between 110° and 220° C. was 23 kilocalories per mole.

Berkowitz (8) observed the DTA curve shown in figure 11b of Klason lignin using an atmosphere of pure nitrogen with a 6°C. per minute heating rate. An exotherm begins at about 200° C., reaches a plateau extending from 290° to 380° C., and undergoes a second exothermic reaction peaking at about 420° C.

Kudo and Yoshida (46) 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 with completion of the reaction at 450° to 500° C.

A heat of reaction of 6 kilocalories per gram for beech lignin was found by Keylwerth and Christoph (41). The thermogram showed an endothermic peak at about 320° C., an exotherm at about 510° C., and an incomplete exotherm continuing beyond 600° C.

Arseneau (4) assumed that the DTA exotherm for acid lignin at 230° C. (fig. 2) was actually evident in the wood thermogram at 265° C., having been displaced because of physical or chemical changes in the extraction process.

Domansky and Rendos (17) compared the DTA curves of different lignin preparations (fig. 11c and d) and concluded that the degradation pattern was practically the same for each. An endotherm extended from about 100° to 180° C., merging into an exothermic stage without a sharp maximum. The maximum occurs for a range from about 280° to 300° C., and is followed by a dimin-

ished second exothermic region peaking at about 400° C. The Nell lignin is prepared by dimethylaniline extraction followed by 78 percent sulfuric acid, and may differ considerably from the Ritter 72 percent sulfuric acid extraction, a refined Klason procedure.

Kollmann and Fengel (45) 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 for this temperature range. Above 150° C., the lignin content of both oak and pine increased, presumably because of chemical reaction of the decomposed hemicelluloses with lignin.

Tang (70) found two stages of first-order decomposition for sulfuric-acid-processed spruce lignin, at 280° to 344° C. and at 344° to 435° C., with activation energies of 21 and 9 kilocalories per mole, respectively. Figure 7a and b contains the TGA and derivative TGA curves, whereas the first-order kinetics curve is shown in figure 7c. The work was conducted *in vacuo* at 3° C. per minute with 10-milligram samples.

Ramiah and Goring (59) obtained decomposition activation energies of 52 kilocalories per mole for dioxane lignin and 108 kilocalories per mole for periodate lignin. Dioxane lignin began decomposing at 130° C., whereas the periodate lignin began at 145° C. The thermal stability of lignin was considered greater than that of the hemicelluloses and less than that of cellulose.

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