THERMOGRAVIMETRIC EVALUATION OF FUNGAL DEGRADATION OF WOOD[1]

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ABSTRACT

Yellow birch (*Betula alleghaniensis* Brit.) was degraded by a white rot fungus (*Polyporus versicolor* L. ex Fr.; now *Coriolus versicolor* (L.) Quél.) and a brown rot fungus (*Poria monticola* Murr.; now *Poria placenta* (Fr.) Cke.) under controlled conditions. Samples of known weight loss from fungi were milled to pass a 40-mesh screen, oven-dried, and then measured for rate of mass loss over selected temperature ranges. Rates of mass loss of nominal 4-mg samples were obtained isothermally in flowing oxygen using a thermogravimetric (TG) system containing a Cahn electrobalance. Activation energy (E) was found using zero-order kinetics for the initial mass loss. White-rotted birch (to 60% weight loss) had an E of 35 to 43 kcal/mole over the range of approximately 190 to 210 C. On the basis of TG data, the weight loss from fungal attack could be predicted within about 5%. Brown-rotted birch had more variation in E (30 to 44 kcal/mole), over a temperature range of 170 to 195 C. The rate of mass loss of brown-rotted birch (to 52% weight loss) was more sensitive to temperature because of the known nonlinear decrease in cellulose DP during fungal attack. Dynamic thermogravimetry, a much simpler method, indicated a similar degree of instability from fungal attack as did the isothermal tests. TG appears to be a viable research method to evaluate fungal attack of wood.

Keywords: Thermal analysis, isothermal TG, dynamic TG, *Betula alleghaniensis*, white rot, brown rot, *Polyporus versicolor*, *Poria monticola*, biodegradation, decay.

INTRODUCTION

The nature of fungal attack on wood, causing depolymerization and volatilization of the macromolecules, suggests that degraded wood might have reduced thermal stability. If thermal stability could be related quantitatively to the degree of fungal degradation, then a nondestructive, microquantity test might be possible to evaluate deterioration of wood in service. Furthermore, such tests could supplement or complement the current exposure tests and wet-chemistry techniques used to evaluate fungal attack.

Thermogravimetry (TG) is a technique for measuring mass loss of a substance under controlled conditions of temperature and atmosphere. Commercial microbalances are available with a sensitivity of ± 1 μg under dynamic (flowing gas) conditions, permitting a very small sample size. During exposure to conditions which cause very small relative mass losses, it is

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possible to evaluate the thermal stability of a material. Since polymeric materials should be less thermally stable if partially depolymerized or fragmented, it was anticipated that TG might be at least a qualitative tool in analyzing fungal attack on wood.

The conventional method for evaluating fungal degradation of untreated wood (ASTM D2017-71) requires that specimens of approximately 6 cm^3 be exposed under controlled conditions to previously inoculated feeder strips. A similar standard (D1413-76) is used to determine the effects of fungi on preservative-treated wood. In each case, weight loss of the specimens is considered as an index of the degree of fungal attack. There are a number of inherent problems in these standards, including procedural difficulties (primarily related to wood moisture content) and exposure time required for consistent results. However, the greatest limitation appears to be in unavoidable development of deterioration gradients and zones within the specimen. Alternative methods have been developed to measure the change of certain strength properties when wood is exposed to fungal attack. These methods introduce problems in specimen preparation (size and shape) and the variability of strength tests. The "average weight loss" determined in standard tests is difficult to correlate with strength loss, particularly during initial fungal attack, when steep deterioration gradients occur in the test specimens. Respiration (oxygen consumption or carbon dioxide evolution) methods have been developed to measure fungal activity more rapidly and obtain preservative threshold levels. (A recent review is provided by Smith 1975.) The problems inherent in this method are very similar to those described for the ASTM standard tests.

The purpose of this study was to determine if fungal attack on a hardwood sufficiently altered its thermal stability to enable evaluation by thermogravimetry. The hypothesis was tested on samples which had been previously prepared by conventional means. In this paper, "weight loss" refers to that incurred from fungal attack, while the term "mass loss" is the loss observed during TG exposure.

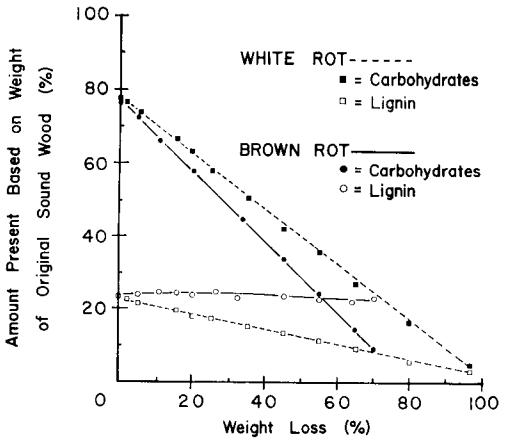

FIG. 1. Total carbohydrate and lignin fractions of initial wood weight of sweetgum sapwood attacked by a white rot fungus (*Polyporus versicolor*) and a brown rot fungus (*Poria monticola*) (Cowling 1961).

BACKGROUND

Fungal attack on wood

Attack of hardwoods by typical white rot fungi such as *Polyporus versicolor* L. ex Fr. (now *Coriolus versicolor* (L.) Quél.) and brown rot fungi such as *Poria monticola* Murr. (now *Poria placenta* (Fr.) Cke.) causes a loss in carbohydrate and lignin fractions as shown in Fig. 1 (Cowling 1961). A major difference in the progression of fungal attack is the relatively unchanged weight fraction of lignin in brown rot. However, within the carbohydrate fraction, cellulose and hemicelluloses are lost uniformly from attack by either fungi.

The change in DP of holocellulose differs considerably with each fungus (Fig. 2). White rot fungi gradually lower the DP to about 80% of the initial value at about 70% weight loss. Brown rot fungi cause a rapid initial decrease in DP from about 1,600 to 200, followed by a gradual decline, in a similar manner to that of acid hydrolysis.

If the cellulose elementary fibril is con-

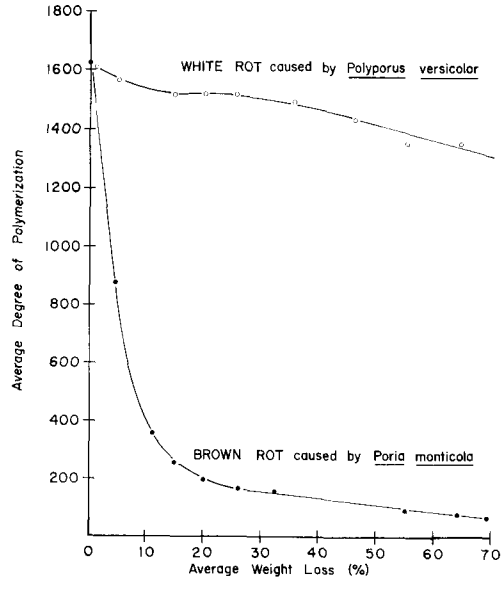

FIG. 2. Average holocellulose DP of sweetgum sapwood attacked by a white rot fungus (*Polyporus versicolor*) and a brown rot fungus (*Poria monticola*) (Cowling 1961).

sidered to be essentially crystalline and indefinite in length, then the characteristic manner of reduction in DP by each fungus may be consistent with its mode of attack. The nominal DP of cellulose in wood is about 10,000, although the value for extracted cellulose may be considerably lower (Timell 1956). Assuming 37 chains per elementary fibril, with randomly distributed chain ends, a point defect in the crystal lattice will occur at a maximum separation of 270 glucose residues. If catalysts involved in attack by brown rot fungi completely penetrate the elementary fibril at these "sensitive points," then cellulose DP would decrease abruptly, producing a series of crystalline fragments. Beyond this, the DP would gradually decrease from endwise attack on the "crystallites." This sequential attack is consistent with brown rot DP curve in Fig. 2. In contrast, white rot fungi apparently degrade the exposed surface chains of the elementary fibrils in an endwise manner with little penetration into the interior, gradually decreasing the cellulose content with little change in average DP of the residue.

Isothermal TG analysis

The rate change in concentration, C, during isothermal decomposition of a material can be expressed by (Flynn and Wall 1966):

$$dC/dt = kf(C), \tag{1}$$

where $C = 1 - m/m_0$,
m = mass at any time, t,
m_0 = initial mass,
k = rate constant.

There are many possible forms of $f(C)$ but the most widely used is

$$f(C) = (1-C)^n, \tag{2}$$

where n is the order of reaction.

Substituting Eq. (2) into (1),

$$dC/dt = k(1-C)^n, \tag{3}$$

and replacing concentration with mass,

$$(1/m_0)(dm/dt) = k(m/m_0)^n, \tag{4a}$$

or

$$-(m_0{}^{n-1})\dot{m}/m^n = k, \tag{4b}$$

where $\dot{m} = dm/dt$.

In the case of very small mass losses, $m \simeq m_o$ and Eq. (4) reduces to

$$-\dot{m}/m_0 \simeq k, \tag{5}$$

which is the same form as Eq. (4) when $n = 0$ for a zero-order reaction.

Therefore, when very small initial mass losses occur, the reaction can be mathematically treated as zero order. The temperature dependence of k is generally expressed as the Arrhenius equation:

$$k = Ae^{-E/RT}, \tag{6}$$

where E = activation energy (cal/mol),
R = gas constant (1.987 cal/mol K),
T = Temperature (K),
A = preexponential factor (5^{-1}).

Substituting Eq. (6) into Eq. (5)

$$-\dot{m}/m_0 = Ae^{-E/RT}. \tag{7}$$

The logarithm of Eq. (7) places it into the conventional form for plotting the data:

$$\ln(-\dot{m}/m_0) = \ln A - E/RT. \tag{8}$$

A plot of $\ln(-\dot{m}/m_0)$ vs. $1/T$ gives a slope of E/R from which E is obtained.

Such an assumption of zero-order kinetics for up to 2% mass loss in this study appears to be valid from previous work. Beall (1968) found a zero-order reaction for up to 20% mass loss of yellow birch heated at 3 C/min in oxygen between 221 and 248 C with an activation energy of 37 kcal/mol.

Dynamic *TG* (controlled rate of heating) can be used to obtain activation energies for the decomposition of reasonably complex compounds, including high polymers. However, wood contains such a mixture of low and high molecular weight substances that simple kinetic schemes are not valid. In degraded wood, the more complex process of molecular decomposition obscures its kinetic relationship to normal wood.

METHODS

Sample preparation

Test specimens consisted of end-matched blocks 20 × 40 × 15 mm cut from the same annual rings of a cant of yellow birch (*Betula alleghaniensis* Brit.). The blocks were randomized, numbered with India ink, oven-dried for 48 h at 60 C, cooled in a desiccator over anhydrous $CaSO_4$, and weighed to the nearest 0.01 g. Each block was then dipped for 5 sec in boiling water for surface sterilization and placed into a soil-block test assembly previously inoculated with either a brown rot fungus (*Poria monticola* Murr.) or a white rot fungus (*Polyporus versicolor* L. ex Fr.). Test assemblies were incubated in diffuse light for 2 to 12 wk. The blocks were removed, gently washed free of fungal mycelium and oven-dried using the previous procedure. Selected blocks were then split into small pieces with a chisel and ground in a Wiley mill to pass a 40-mesh (425 μm) screen. Control specimens were treated in exactly the same manner except they were placed in soil-block jars which had not been inoculated with a fungus.

TG system

The sample crucible was suspended from a Cahn microbalance with a nichrome wire. Oxygen was metered through a vycor tube, exiting via an oil bubbler. Changes in sample mass (±1 μg) were converted to a recorded voltage output using standard Cahn equipment. A Valley Forge temperature controller, with proportional control and a platinum resistance sensor, provided constant rate or isothermal heating from the split-element Cahn furnace. Sample temperature was continuously recorded at 2 mm below the crucible (simultaneously recorded with mass on a two-channel strip-chart recorder) using a type-K (Chromel/Alumel) thermocouple and a solid-state reference junction.

TG runs

Preliminary TG runs on controls were made separately in nitrogen and oxygen. At low temperatures, the rates of mass loss were approximately the same in each atmosphere, indicating volatilization as the dominant mechanism. At higher temperatures, the effect of oxidation increased, producing a rate of mass loss in oxygen about twice that as in nitrogen. Oxygen was then used in all subsequent test runs to take advantage of the increased sensitivity of the system.

Constraints in selection of an isothermal temperature for the samples were: (1) the temperature should fall within a well-defined zero-order activation energy region for all samples; (2) the mass and rate of mass loss of the control should be high enough to produce the degree of accuracy required in the data analysis; (3) rate of mass loss of the most degraded sample should not be so great that a constant rate is not obtained. Samples must be degassed (including removal of water vapor) at a lower temperature to prevent sorbed gases from interfering with the rate of mass loss from deterioration.

TG samples of nominal 4 mg mass were randomly selected from the milled material and placed in a hemispherical 9-mm-diameter platinum crucible. The TG system was then flushed with oxygen for 15 min at 0.5 L/min (8000 mm^3/sec) equivalent to three volumetric changes of gas, which was

TABLE 1. *Regression equations for TG rate-of-mass loss for isothermal runs*

Sample[a]	Weight loss(%)	Holocellulose content[b](%)	Runs	Regression equation[c] ℓn Y=	s	R^2[d]	Activation energy(kcal/mol)
Control	0	80	7	38.51 - 17.27X	0.146	94.3	34.5
19W	18.5	64	5	46.31 - 20.76X	0.169	93.1	41.5
39W	38.6	48	5	52.11 - 23.40X	0.146	96.2	46.8
51W	51.2	38	5	44.46 - 19.73X	0.149	94.8	39.5
62W	61.5	30	5	44.27 - 19.59X	0.144	94.6	39.2
16B	16.0	60	4	49.12 - 22.08X	0.120	98.3	44.2
25B	25.2	47	5	48.36 - 21.62X	0.129	96.6	43.2
31B	30.9	39	5	48.29 - 21.14X	0.172	95.9	42.3
32B	31.5	38	4	38.27 - 16.48X	0.046	99.1	33.0
42B	42.1	25	4	35.28 - 15.01X	0.048	98.8	30.0
49B	49.1	14	5	41.33 - 17.49X	0.186	95.8	35.0

[a] W = white rot, B = brown rot (sample number is nominal weight loss)

[b] Estimates from previous yellow birch samples for white rot and sugar maple for brown rot (Merrill 1975, private communication)

[c] Y = % mass loss/hr
X = $10^3/T(K)$

[d] The R^2 values are for comparative purposes only since they were obtained from transformed semilogarithmic data

reduced to 0.1 L/min (2000 mm^3/sec) when the run started. For isothermal runs, the sample was exposed to 120 C until the mass stabilized, usually within 30 min. The programmer was then adjusted to raise the temperature at 50 C/min to a preselected isothermal level. Dynamic runs at 1 C/min were made from room temperature to the endpoint temperature. At the end of each run, the residual sample was discarded and the crucible cleaned by firing in air at about 600 C.

RESULTS AND DISCUSSION

Table 1 gives the characteristics for all samples used in the study. The sample identification number consists of the nominal weight loss due to decay plus a letter designation for the type of rotting fungus. Holocellulose contents from other studies are shown for comparative purposes only.

Isothermal TG

The information from isothermal runs is plotted in Fig. 3, with regression equations and statistical data given in Table 1. The temperature limits for brown rot (BR) and white rot (WR) rates of mass loss were established by the criteria discussed in the previous section. The rate of mass loss data was acquired on blind samples within each group (WR, BR). Brown rot of 31% or greater weight loss clearly separated from the WR runs. However, on the basis of rate of mass loss, the WR data were not separable from BR. Although the variation in the data was large, it was possible on the basis of the regression equations to clearly identify the weight loss group for individual samples.

Both BR and WR samples were more clearly separated at the lower end of their respective temperature ranges (about 175 and 190 C), with the exception of sample

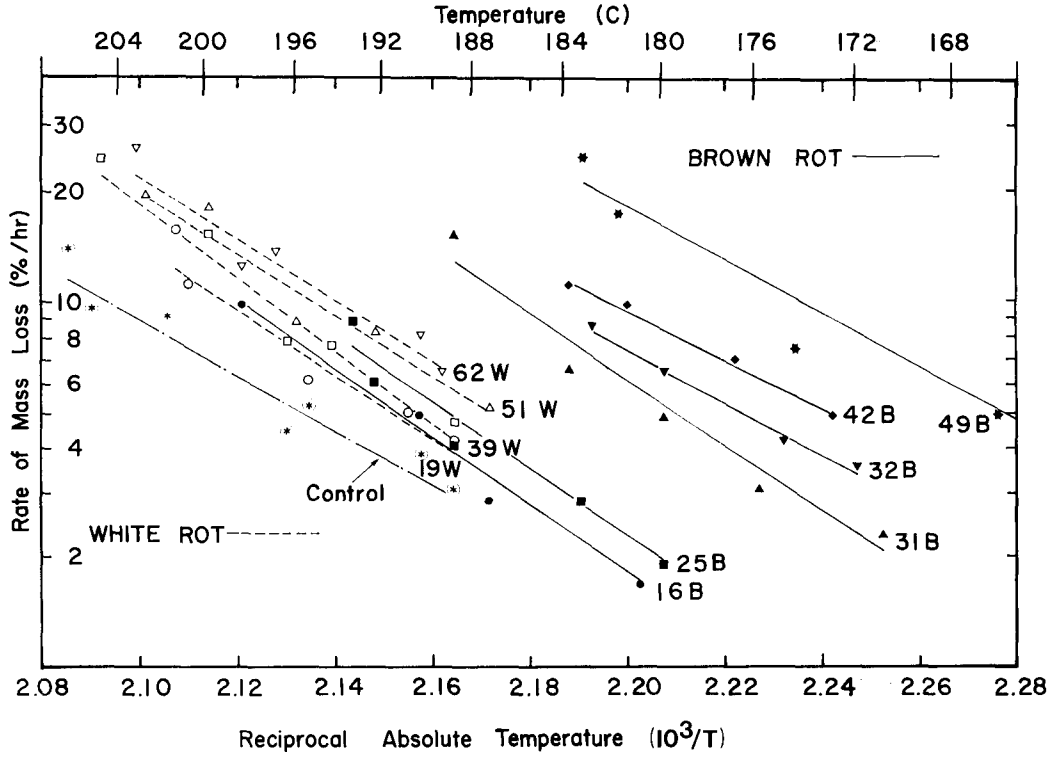

FIG. 3. Data points and regression lines for isothermal decomposition of white-rotted (open symbols) and brown-rotted (filled symbols) yellow birch. Equations and other data are shown in Table 1.

16B. In general, it appeared that even clearer separations could be obtained with each group at the lower temperature limit for the most degraded samples, and at the higher limit for the least. It was not possible to obtain a meaningful relationship between weight loss from fungi and rate of mass loss in TG for either group because of the variation in slope for individual regression equations. The relative uniformity of the WR data suggests that it might be possible, with additional data, to obtain a regression model of the form $\ln Y = Aw - B/T$.

Variability in the data could be attributed to instrumentation, analysis, and sample composition. Thermocouple repeatability could be the major source of error in temperature determination since relative temperature (between runs) was much more important than absolute values. It was believed that temperature error was second-order when compared with the error in subjective determination of rate of mass loss from the chart paper. Fortunately, even a ±10% variation in the slope measurements would not have substantially changed the regression lines. The error in sample mass produced by the flowing gas (buoyancy) was not a factor since it is constant for isothermal runs and was subtracted out in the comparative data analysis for dynamic runs. Sample composition was also a possible source of variability. Even though each replicate was obtained after thoroughly mixing the milled sample, no systematic study was made of the effect of particle size distribution for a replicate. It is known that the particle size produced in milling depends on the degree of fungal degradation of wood. Since the rate of mass loss in TG is inversely dependent on parti-

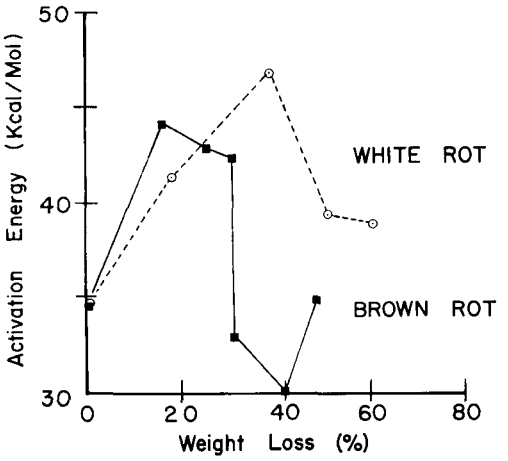

FIG. 4. Activation energy obtained from slope of regression equations in Table 1 for white- and brown-rotted yellow birch of various weight losses.

cle size (surface to volume ratio is a major factor), it might be anticipated that more variability would have occurred among samples than replicates of samples. Even though the samples in this study are identified according to average weight loss from fungal exposure, it is important to realize that there may be large differences in deterioration within a sample. The material in each TG sample, then, contains a distribution of degraded material. Indirect evidence from data variability suggests that the distribution shifts in a complex manner over the range of weight loss in this study.

The activation energies given in Table 1 and Fig. 4 are average values for each sample type over the full temperature range. Because of the limited number of replicates, it was not possible to determine the more detailed variation of E within the temperature range. The usefulness of absolute values of such average activation energies may be questionable because of (1) the number and complexity of degradation schemes for the polymers in wood, (2) specific equipment characteristics and variability with temperature changes, and (3) method of analysis. However, an earlier study of zero-order decomposition of the same species using dynamic TG, a different means of analysis, and much different equipment produced a value which was within 7% of the values in this study (Beall 1968). Both the magnitude and temperature range of E from the earlier dynamic study were similar to the isothermal data, supporting the reproducibility of TG techniques. For both white rot and brown rot, the peak value of E is reached very close to the inflection point of the DP vs. weight-loss curve (Fig. 2). (With brown rot, the peak may occur before 16% weight loss.) An increase in activation energy may be viewed as a decrease in thermal stability. The increase of E for BR from 40 to 49% weight loss may indicate a decrease in lignin stability, corresponding to the slight change in slope in Fig. 1, perhaps from a greater sensitivity of side groups to fragmentation.

Dynamic TG

The major shortcomings of isothermal TG were the number of runs needed per sample, the subjective nature of mass loss measurement, and the lack of a clear separation of WR from BR except for the more degraded BR. In addition, isothermal TG is susceptible to a multitude of repeatability errors. In preliminary work, dynamic TG was used to determine the temperature limits for the isothermal study. At that time, no distinct differences were observed among samples. However, after the isothermal runs were completed, a series of dynamic runs (two replications) were made at the limit of mass resolution of the Cahn balance. The analog data (mass, temperature) were digitized, normalized, and computer-processed to obtain *differences* at given temperatures between the degraded and control samples. The complete set of difference curves is given in Fig. 5, with the control mass as the baseline. The ordinate represents percentage differences between normalized masses and the control. (The actual mass loss of the control at 209 C was about 3.5%.)

When Fig. 5 is compared with Fig. 3, the same types of patterns and groupings found

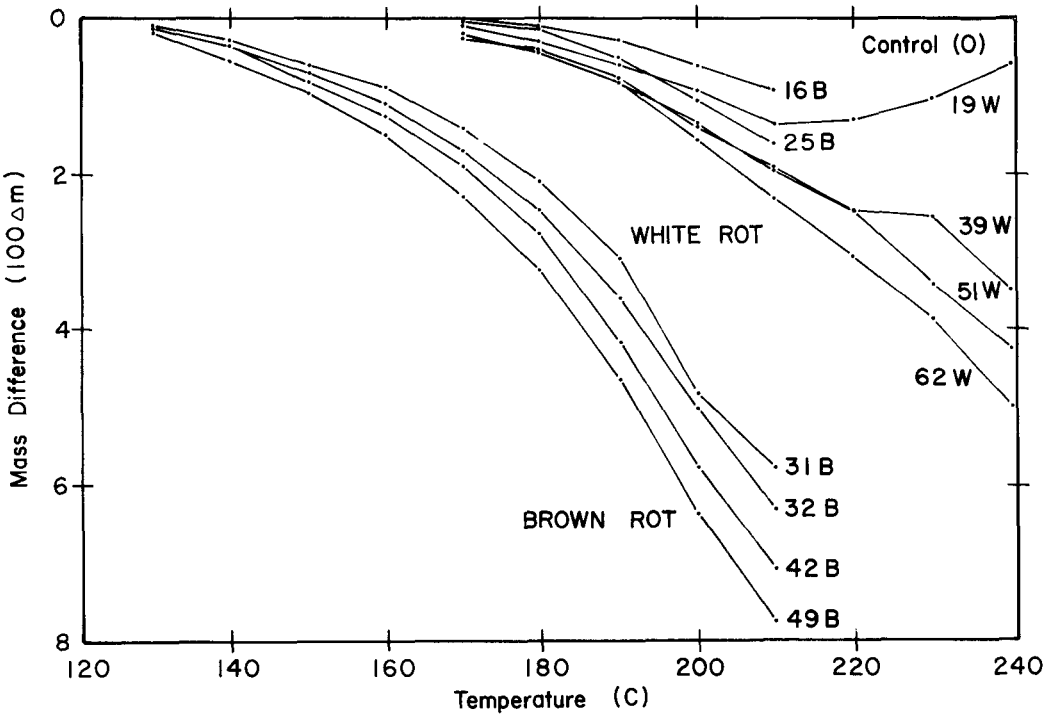

FIG. 5. Dynamic TG of white- and brown-rotted yellow birch adjusted for a zero baseline of the nondegraded control.

in the isothermal study are evident. When the curves of 16B and 25B are compared with 31B through 49B, the latter group is noticeably less stable at lower temperatures, strongly suggesting that a major decrease occurred in cellulose DP between 25 and 31% weight loss. The dynamic TG curves of samples 16B and 25B overlap the WR curves as also observed with the isothermal runs. Reliability in replicate sampling, which could not be checked in the isothermal procedure, was confirmed by a very small variation in the duplicate dynamic runs (generally less than 1%). Although dynamic TG was used as a qualitative tool, such thermograms can be quantitatively compared using the area between curves as an index of thermal stability. It appears that dynamic TG could be especially useful in rapidly and effectively analyzing relative degrees of deterioration of fungal-attacked samples.

TG vs. other methods

The standard soil block test and most alternatives, described in the introduction, have a common disadvantage—relatively large sample sizes. When dimensions are reduced to minimize degradation gradients, data reliability is also lowered. This is especially evident in evaluation of strength losses where both preparation and testing of small samples may cause large uncertainty in results.

The sample mass in this study was approximately one-thousandth of that in the standard soil block test. This could permit the use of microtomed wood specimens to obtain true rather than average deterioration values and to evaluate decay gradients in larger samples. If fully developed as a research tool, it could provide information on relative or even absolute polymeric integrity as interpreted through thermal stability.

CONCLUSIONS

Under the conditions of this study, it was possible to detect differences in thermal stability of fungal-attacked yellow birch, specifically:

1. Individual white and brown-rotted samples could be separated on the basis of sensitivity to temperature, except for brown-rotted samples of less than 31% weight loss.

2. Activation energies obtained from Arrhenius plots of isothermal data appeared to be relatable to fungal degradation of the wood constituents.

3. Dynamic TG, under maximum system sensitivity, provided a rapid semiquantitative measure of thermal stability.

REFERENCES

BEALL, F. C. 1968. Thermal degradation analysis of wood and wood components. Ph.D. thesis, SUNY Coll. of For., Syracuse, N.Y. 240 pp.

COWLING, E. B. 1961. Comparative biochemistry of the decay of sweetgum sapwood by white-rot and brown-rot fungi. USDA Tech. Bull. No. 1258. 79 pp.

FLYNN, J. H., AND L. A. WALL. 1966. General treatment of the thermography of polymers. J. Res. NBS 70 A (6): 487–523.

SMITH, R. S. 1975. Respiration methods to follow wood decay and evaluate toximetric potential of wood preservatives. Mat. Organ. 10(4): 241–253.

TIMELL, T. E. 1965. Wood and bark polysaccharides. Pages 127–156 *in* W. A. Côté, ed. Cellular ultrastructure of woody plants. Syracuse Univ. Press, Syracuse, N.Y.