

Effects of Various Parameters in Differential Scanning Calorimetry of Hydrogen-Peroxide-Treated Lignocellulose

TINH NGUYEN,* EUGENE ZAVARIN, and EDWARD M. BARRALL II,†
*University of California, Forest Products Laboratory, Richmond, California
94804*

Synopsis

Differential scanning calorimetric (DSC) analyses of mixtures of hydrogen peroxide and lignocellulosic materials have been performed. The influence of chamber atmosphere composition, heating rate, pinhole size, lignocellulose particle size, and hydrogen peroxide-to-lignocellulose ratio were examined. With the exception of particle size, the variables produced significant effects on the DSC curves. These effects were mainly connected with changes in the atmosphere surrounding the sample, sample density, heat capacity, and heat conductance.

INTRODUCTION

Differential scanning calorimetric analysis (DSC) of hydrogen peroxide and hydrogen-peroxide-treated lignocellulose was described in our previous two reports.^{1,2} The samples were run at an elevated pressure in deactivated, hermetically sealed aluminum pans with a top pinhole. As with any transition process resulting from thermal treatment, numerous operational factors affect the nature and accuracy of thermal analysis. This report considers the impact of the major factors affecting determination of the thermal characteristics of H₂O₂ decomposition and reactions between H₂O₂ and lignocellulosic materials, including the composition of the chamber atmosphere, heating rate, pinhole size, particle size of lignocellulose, and hydrogen peroxide-to-wood ratio.

EXPERIMENTAL

Unless otherwise stated, all materials used, methods of sample preparation, thermal analytical instrumentation, and operational procedures were the same as described in our previous report.² The DSC analyses were run using plain aluminum pans, deactivated by soaking in boiling 15% HNO₃ for 0.5 h followed by soaking in boiling 50% H₂O₂ for 1 h, and finally washed several times with boiling water. The hermetically sealed pans were provided with a top pinhole between 0.050 and 0.065 mm in diameter. Prior to analysis the sample cell was purged with an appropriate gas at a flow rate of 50 mL/min at atmospheric or higher chamber pressures. The DSC runs were carried out at 975 psi pressure and 20°/min heating rate in nitrogen or oxygen atmospheres.

* Present address: ARCO Chemical Co., Newtown Square, PA 19073.

† Present address: IBM, San Jose, CA 95193.

RESULTS AND DISCUSSION

Atmosphere of the Sample Chamber

It is well known that the rate and mechanism of reactions studied by DSC and involving lignocellulosic materials depend strongly on the composition of atmosphere immediately surrounding the sample and also within the chamber containing the sample holder. Atmospheric gases may react with the sample or displace volatile products of the reaction(s), changing the course and/or extent of reactions between such volatile products and the nonvolatile sample components. It is desirable, therefore, to control the composition of both the bulk gas and the gas immediately surrounding the sample. Unfortunately, due to the volatility of H_2O_2 solution, it is impossible to remove the air entrapped in the sealed sample holder without changing the H_2O_2 concentration in the sample. Therefore, only the composition of the bulk gas was controlled in this study.

Figures 1 and 2 and Table I show DSC results for H_2O_2 -treated wood, lignin, cellulose, and pinitol (5-O—methyl *d*-inositol) run in N_2 or O_2 . The figures for specific areas (area/ H_2O_2 wt) represent averages of two measurements. As described in our previous report, the first exotherm is apparently due to two reactions, H_2O_2 decomposition to form oxygen and water and reaction between H_2O_2 and lignocellulose. As evidenced by Table I, the onset temperature T_0 and the peak temperature T_1 were unaffected by changing from pressurized N_2 to pressurized O_2 . However, such a change considerably reduced the T_1 peak area and height. In the case of the T_2 peak, shifting from N_2 to O_2 atmosphere increased the T_2 peak temperature for H_2O_2 -treated wood from 234.5°C to 253°C, while reducing the same for H_2O_2 -treated cellulose from 251°C to 235°C. This indicates that cellulose is more susceptible to oxidation than lignin-carbohydrate complexes. Even more striking were the large increases in T_2 peak areas in the case of H_2O_2 -treated wood and cellulose and the appearance of a second exotherm

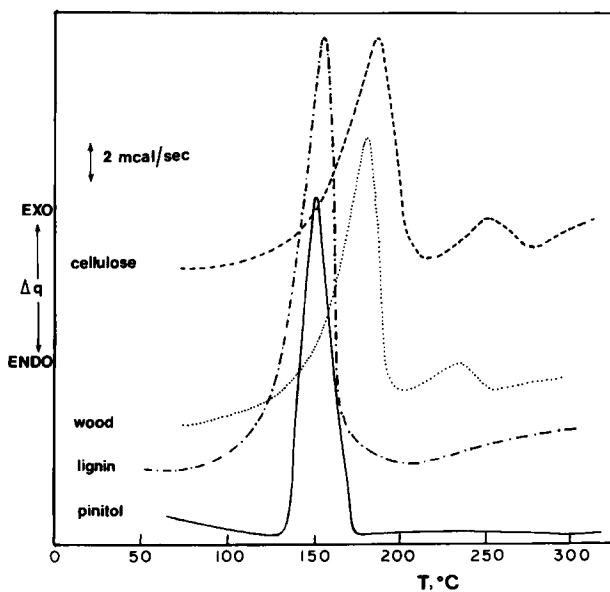


Fig. 1. DSC of H_2O_2 -treated lignocellulose in N_2 ; sample size, 1.42 mg.

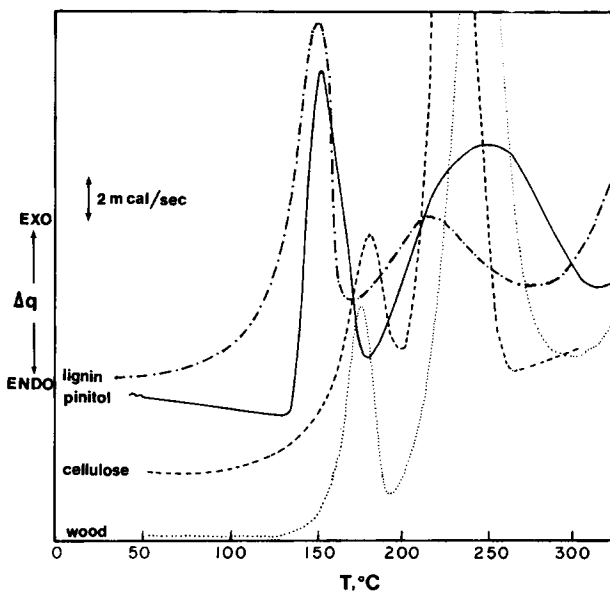


Fig. 2. DSC of H₂O₂-treated lignocellulose in O₂; sample size, 1.42–3.55 mg.

(T_2) in the cases of H₂O₂-treated lignin and pinitol now partially overlapping the first exotherm.

With H₂O₂-treated cellulose and wood, the enhancement of T_2 peak areas in O₂ indicates that the second exothermal reaction involves oxygen. This is supported by the appearance of the second exotherm in DSC of H₂O₂-treated lignin and pinitol run in O₂ atmosphere. The much larger T_2 peak areas associated with H₂O₂-treated wood and cellulose as compared to H₂O₂-treated lignin in O₂ suggest that carbohydrates are primarily responsible for the second exothermal reaction in N₂.

Table I also includes data on the thermal characteristics of H₂O₂ decomposition in N₂ and O₂ atmosphere. The results indicate that, although the maximum decomposition temperature of H₂O₂ (50% w/w) was unaffected by shifting from N₂ to O₂ atmosphere, such a change decreased the onset temperature (T_0).

Heating Rate

Heating rate can assume a major importance when studying chemical reactions by thermal analysis.^{3,4} The results shown in Figures 3, 4, and 5 indicate that increasing the heating rate from 10°C/min to 50°C/min does not significantly affect the characteristics of the first or second exotherm obtained by DSC of H₂O₂, H₂O₂-treated lignin, or H₂O₂-treated carbohydrates in N₂. However, DSC of carbohydrates run at slower heating rates of 2–5°C/min, while showing the first exothermic peak similar to that obtained at higher heating rates, does not show the second exothermic peak.

The absence of the second exothermic peak at slower heating rates in N₂ is consistent with the work of Johnson and Miller,⁵ who suggested that faster heating rates may sometimes be required to observe minor reactions not detectable at slower heating rates. Interestingly, the second exothermic peak is

TABLE I
Thermal Behavior of H₂O₂ and H₂O₂-Treated Lignocellulosic Materials in N₂ and O₂^a

Materials	First peak			Second peak		
	Onset temp. T ₀ (°C)	Peak temp. T ₁ (°C)	Specific area (cm ² /mg H ₂ O ₂)	Peak temp. T ₂ (°C)	Specific area (cm ² /mg carbohy.)	
H ₂ O ₂ -treated						
in nitrogen	Lignin (brown rot)	125	154	48.91	—	—
	Wood (extractive free, white fir)	147.5	182	37.94	232	2.81 ^b
	Cellulose (microcrystalline)	151	186	35.97	250	2.12
	Arabinoxylan	122.5	140	37.76	202	6.91
	Pinitol	135	152	32.66	—	—
	Glucose	103	135	36.35	244	3.71
	H ₂ O ₂ (50 wt %)	137	187	14.11		
Wood exo. shoulder at 330–370°C, endo. peak at 385°C, exo. peak at 405°C, exo. shoulder at 435–470°C						
H ₂ O ₂ -treated						
in oxygen	Lignin	126	153	39.51	220	8.76 ^c
	Wood	157	182	29.11	253	33.65 ^b
	Cellulose	153	185	28.33	235	46.90
	Pinitol	135	152	31.90	234	8.10
	Glucose	118	140	29.63	238	27.25
	H ₂ O ₂ (50 wt %)	126	183	13.47		
Wood exo. peaks at 339°C and 477°C						

^a Heating rate: 20°C/min, pressure: 975 psi, pinhole plain aluminum pan.

^b Assuming 75% of white fir is carbohydrate.

^c Based on lignin.

observed with H₂O₂-treated materials at all heating rates examined, when DSC is performed in O₂ (Figs. 6 and 7). The absence of the second exothermic peak at lower heating rates in N₂ suggests that the second exothermic reaction is not only a function of carbohydrate content, but also of O₂ supply. The oxygen may result from the thermal decomposition of hydrogen peroxide (2H₂O₂ → 2H₂O + O₂) or could also be a product of some reaction between hydrogen peroxide and lignocellulose. Apparently at slower heating rates, the rate of O₂ production is too slow, compared to the rate of O₂ exchange with the surrounding N₂ atmosphere, to permit a significant oxygen-carbohydrate reaction. Such a reaction is observed at higher heating rates, where O₂ is produced faster and becomes available for the reaction prior to exchange.

Pinhole Size

The structure of the sample holder is extremely important to DSC of materials such as H₂O₂-treated wood where volatile products are formed during analysis. In this case, the shape and thermal characteristics of DSC curves are determined by the temperature dependent rate of H₂O₂ evaporation. The DSC results depend also on the size of the opening in the top of the sample holder through which reactive vapors escape during analysis. The size of the opening regulates also

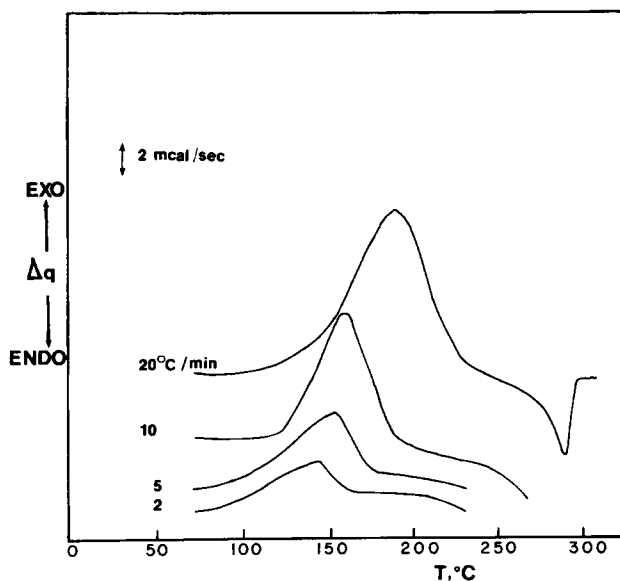


Fig. 3. DSC of 50 wt % H₂O₂ at different heating rates in N₂; sample size, 1.89 mg.

the extent to which volatile products are displaced by purging gas. Specifically in the case of H₂O₂-treated wood, the size of the pinhole can influence the reaction of carbohydrate components of wood with O₂ produced from H₂O₂ and represented by the second exothermic peak observed between 220–250 °C at 975 psi, in N₂ atmosphere.

The effect of the size of the pinhole on the DSC characteristics of H₂O₂-treated wood in N₂ at atmospheric pressure is shown in Figure 8. Increasing the pinhole size from 0.050 to 0.255 mm resulted in broadening of the evaporation endotherm and a lower evaporation initiation temperature for the aqueous H₂O₂ component

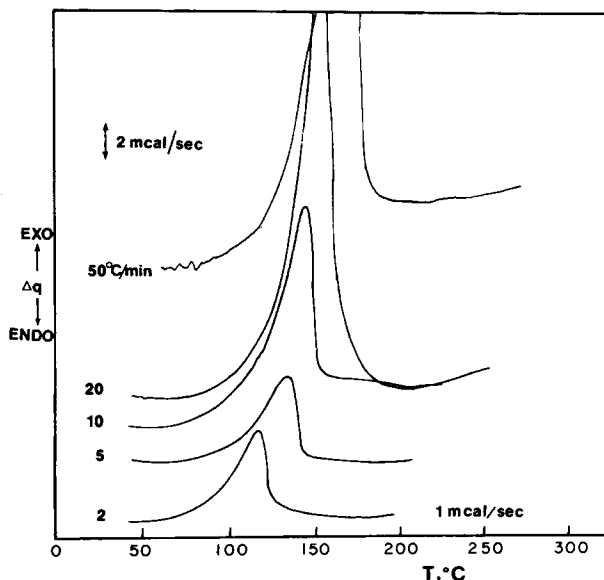


Fig. 4. DSC of H₂O₂-treated lignin at different heating rates in N₂; sample size, 1.89 mg.

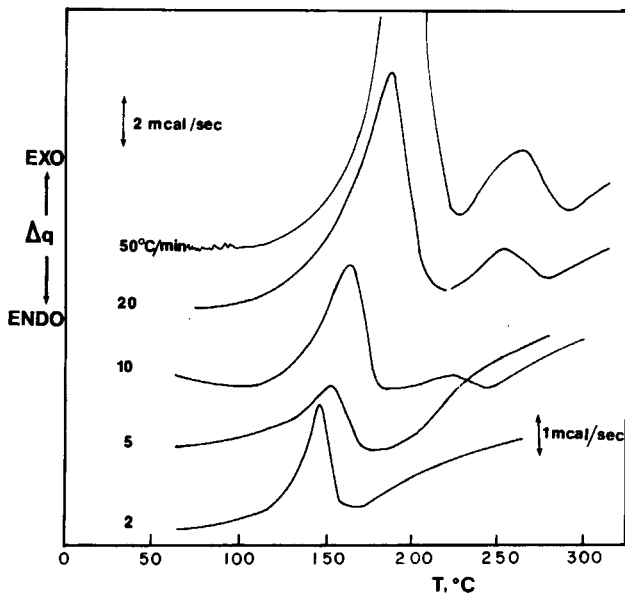


Fig. 5. DSC of H₂O₂-treated cellulose at different heating rates in N₂; sample size, 1.89 mg.

of the system. The evaporation initiation temperature was lowered even more when the sample pan was opened. Increasing the pinhole size also had a striking effect on the characteristics of the first exothermal peak, which occurred at 160°C under atmospheric pressure. As mentioned previously, this exotherm results

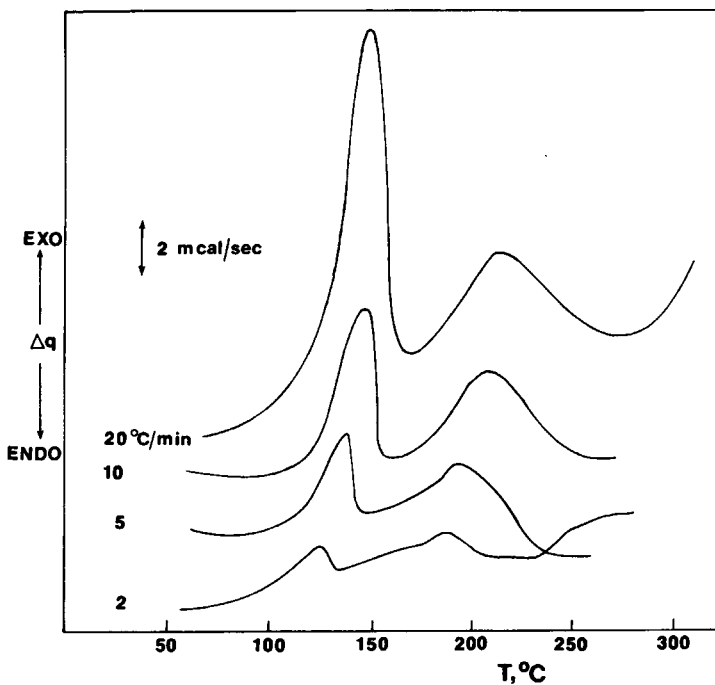


Fig. 6. DSC of lignin at different heating rates in O₂; sample size, 1.89 mg.

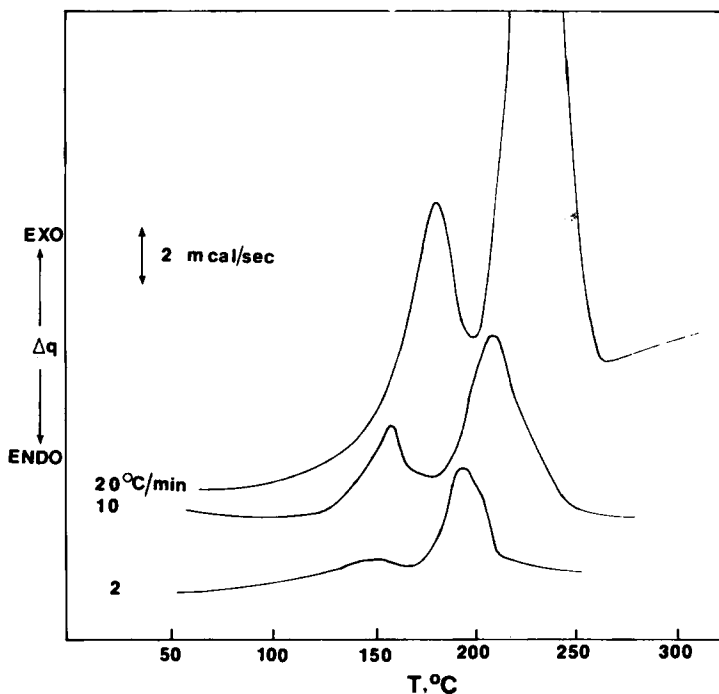


Fig. 7. DSC of cellulose at different heating rates in O₂; sample size, 1.89 mg.

from two reactions, decomposition of H₂O₂ vapor and reaction of H₂O₂ vapor with wood. As the pinhole size was increased, the size of this exothermal peak (area per unit weight of H₂O₂) decreased to the point of its disappearance in the case of the open pan. These findings indicate that larger pinhole openings allow

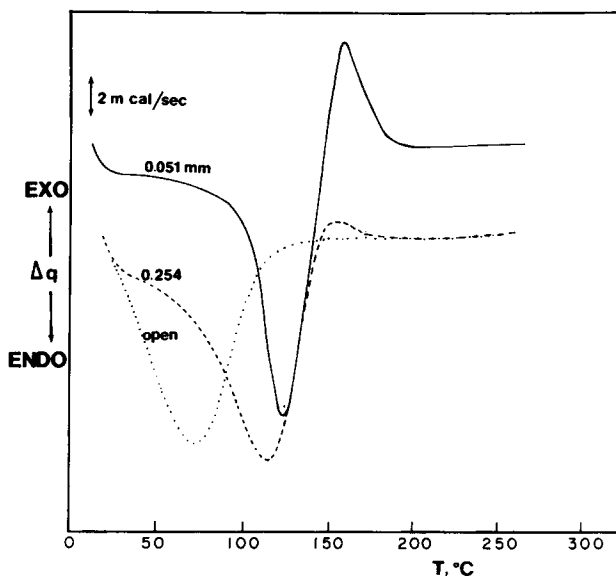


Fig. 8. DSC of H₂O₂-treated wood at different pinhole sizes, in N₂, at ambient pressure; sample size, 1.89 mg.

greater amounts of H_2O_2 vapor to escape from the sample holder yielding less H_2O_2 vapor available for decomposition or reaction with wood.

At 975 psi, and in either N_2 or O_2 , the effect of pinhole size on the first exothermal peak of H_2O_2 -treated wood differed from that observed for N_2 at ambient pressure. Figures 9 and 10 show that the shape and area of the first exotherm when measured at 975 psi did not significantly change when the pinhole size was varied from 0.050 to 1.125 mm in N_2 atmosphere or from 0.050 to 1.143 mm in O_2 atmosphere. However, larger openings affected the shape and area of this peak. Thus, with an opening of 1.990 mm the first exothermal peak in either N_2 or O_2 atmosphere became broader and less sharp. Moreover, when the pan was completely open, the sharp exotherm observed with pinholes below 1.125 mm became an extended exothermal shoulder.

The size of the pinhole did not significantly affect the shape or area of the second exothermal peak of H_2O_2 -treated wood when run in O_2 at 975 psi; however, it did so in N_2 (Fig. 9). In this case, as pinhole size was increased from 0.060 to 0.635 mm, the peak areas decreased. For a 0.635-mm pinhole, the second exothermal peak occurred only as a shoulder, and, with the pan completely open, no second peak was observed at all. Since the second exothermal peak results from the reaction of wood components with O_2 , either trapped in the sample pan or produced during the first exothermal reaction(s), these results indicate that the available oxygen is gradually displaced from the pan atmosphere by the surrounding N_2 , the displacement taking place more rapidly at larger pinhole openings.

The results are consistent with the findings of Miller and Turner,⁶ who analyzed by DTA the thermal behavior of cellulose at ambient pressure in N_2 atmosphere. When the sample was encapsulated in air using a sealed sample pan provided with a top pinhole, they observed a small exothermal peak at 325°C; this peak was absent, however, when the sample pan was completely open or when

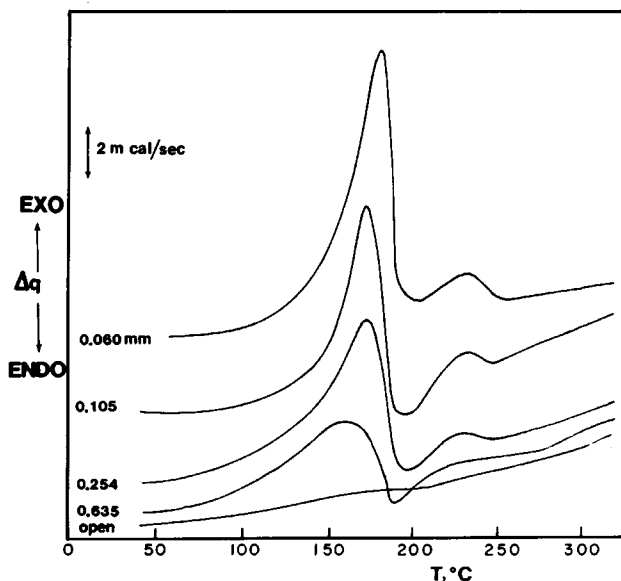


Fig. 9. DSC of H_2O_2 -treated wood at different pinhole sizes, in N_2 , at 975 psi pressure; sample size, 1.89 mg.

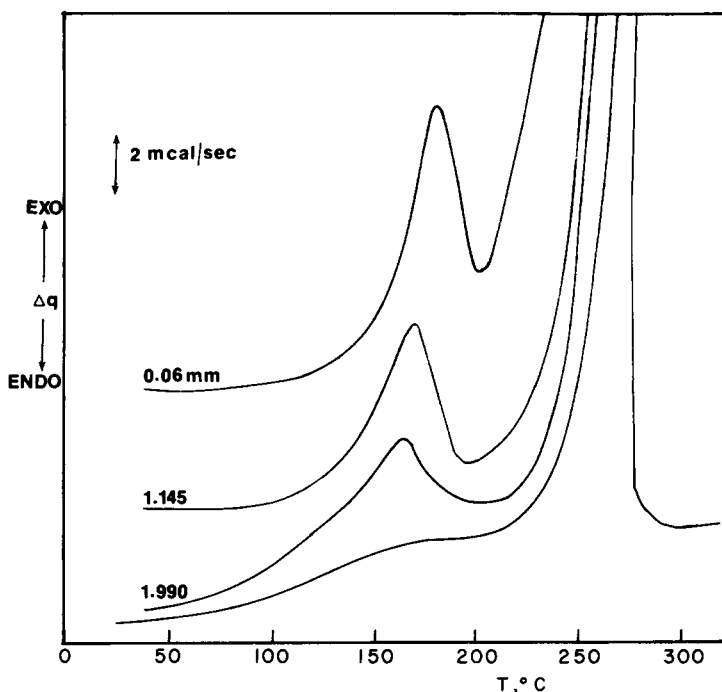


Fig. 10. DSC of H₂O₂-treated wood at different pinhole sizes, in O₂, at 975 psi pressure; sample size, 1.89 mg.

the sample was encapsulated in N₂. The difference between the chamber pressure used in the present study (975 psi) and that used in the study of Miller and Turner (14.7 psi) explains the difference between the exothermic peak temperatures observed. The difference in the magnitude of the exotherm observed at 325°C by Miller and Turner and the magnitude of the exotherm observed at 220–250°C in the present study can be also explained by taking into account the relative amounts and concentrations of O₂ available for reaction with carbohydrate macromolecules. In the Miller and Turner work, trapped O₂ was the only source of O₂, while, in the present work, O₂ resulted also from the H₂O₂ reactions.

A discussion of the influence of the condition of the top of the sample holder

TABLE II
Effect of Particle Size on DSC Characteristics of Hydrogen-Peroxide-Treated Wood^a

Particle mesh size	First peak			Second peak	
	Onset temp (°C)	Peak temp (°C)	Specific peak area (cm ² /mg H ₂ O ₂)	Peak temp (°C)	Specific peak area (cm ² /mg OD wood)
<200	145.5	171.0	34.415	221.0	1.324
80–100	154.0	173.0	34.415	227.5	1.580
60–80	147.5	175.5	37.532	229.0	1.616
40–60	145.5	175.0	39.979	231.5	2.209
20–40	144.0	178.0	39.431	229.0	1.616

^a Heating rate: 20°C/min; pressure: 975 psi; pinhole plain aluminum pan; sample weight, 1.89 mg.

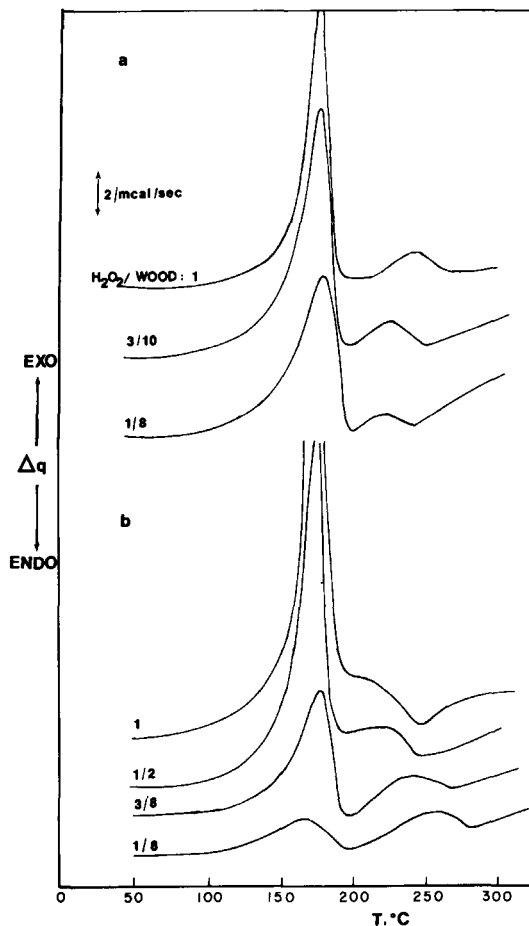


Fig. 11. DSC of samples with different H_2O_2 /wood ratios, (a) constant amount of H_2O_2 and (b) constant total sample weight; N_2 atmosphere; sample size, 1.05–3.55 mg.

on DSC of the decomposition of various fibers in air and in N_2 at ambient pressure is included in the work by Ennis.⁷

Particle Size

Particle size of samples is an important parameter in thermal analysis, particularly in characterization of chemical reactions. As a general rule, chemical reactivity increases as particle size decreases. In DSC, this is evidenced by a sharpening of the peaks as the particle size is decreased. DSC peak area is also inversely proportional to thermal conductivity of the sample which depends in turn on both particle size and packing density.⁸

Table II presents results showing the effect of particle size on DSC characteristics of H_2O_2 -treated wood. The experiments were made by thoroughly mixing five parts vacuum/oven-dried samples of deionized wood of different particle sizes (i.e., <200 to 20–40 mesh) with three parts 50% w/w H_2O_2 in the manner described in our previous paper.¹ The treated samples were stored at

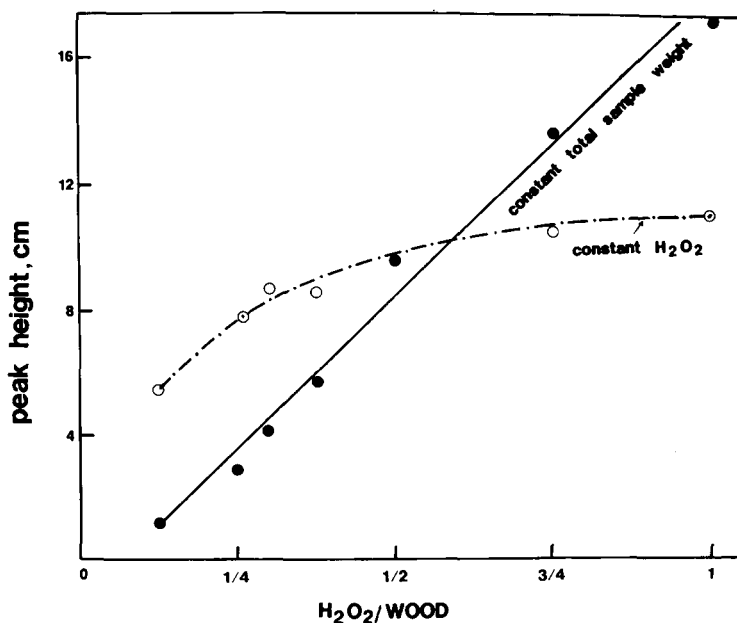


Fig. 12. Relationship between peak height and H₂O₂/wood ratio. First exothermal peak.

ambient temperature for 16 h in closed weighing containers prior to the runs. The results showed no major differences between the thermal behavior of H₂O₂-treated wood in the range of particle sizes of <200 to 20–40 mesh, although there was a discernible slight drop in the maximum peak temperatures and peak areas with a decrease in particle size for both exothermal (T_1 and T_2) reactions.

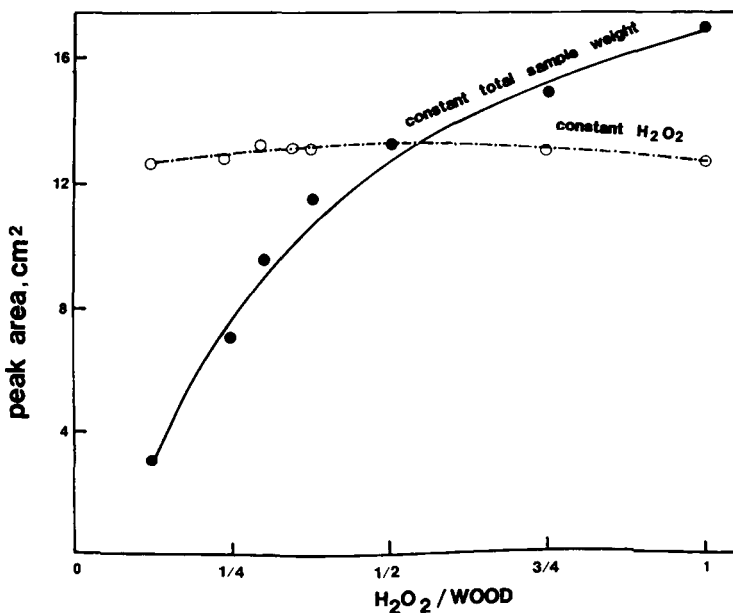


Fig. 13. Relationship between peak area and H₂O₂/wood ratio. First exothermal peak.

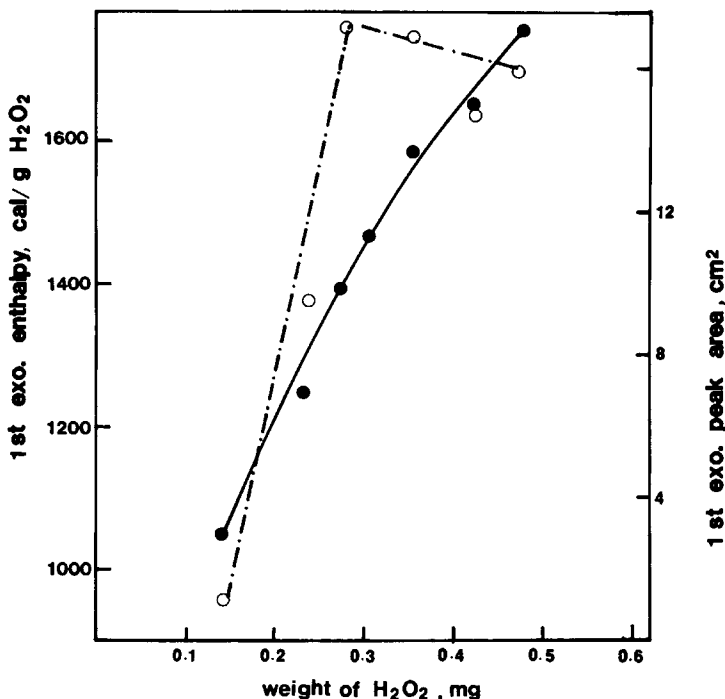


Fig. 14. Dependence of enthalpy and peak area on the amount of H_2O_2 at a constant total sample weight = 1.42 mg. First exothermic peak. (—●—) Area; (- - ○ - -) enthalpy.

H_2O_2 -Lignocellulose Ratio

For investigation of the influence of concentration of the reactants, the deionized 60–80 mesh wood samples were extracted with boiling alcohol and water, mixed with 50% w/w H_2O_2 at different H_2O_2 /wood ratios and stored at ambient temperature in a closed weighing container for 8 h before thermal analysis. Mixtures of H_2O_2 and wood were prepared either by adding a constant amount of H_2O_2 (equivalent to 0.35 mg of anhydrous H_2O_2) to different quantities of wood (method 1), or by adding different quantities of H_2O_2 to wood to produce a constant total sample weight (method 2). The effect of the H_2O_2 /wood ratio on the thermal characteristics of H_2O_2 -treated wood is shown in Figures 11–15 (N_2 atmosphere).

With samples prepared by method 1, varying the H_2O_2 /wood ratio between 1/8 and 1 resulted in little or no effect on the first exothermic peak area, temperature or enthalpy (Fig. 13). At the same time, increase in the H_2O_2 /wood ratio resulted in an enhanced reactivity, as evidenced by peak sharpening with the peak height increasing with an increasing H_2O_2 /wood ratio up to a ratio of 1/2, and then remaining relatively constant (Figs. 11 and 12). Varying the H_2O_2 /wood ratio between 1/8 to 1 slightly increased the maximum temperature of the second exothermic peak without affecting its shape or area (Fig. 15). The lower peak temperatures of the second exotherm observed at lower H_2O_2 /wood ratios can be accounted for by the relatively greater proportion of carbohydrates.

When H_2O_2 -wood mixtures of different constituent ratios were prepared to yield a constant total sample weight (method 2), considerable variation in the

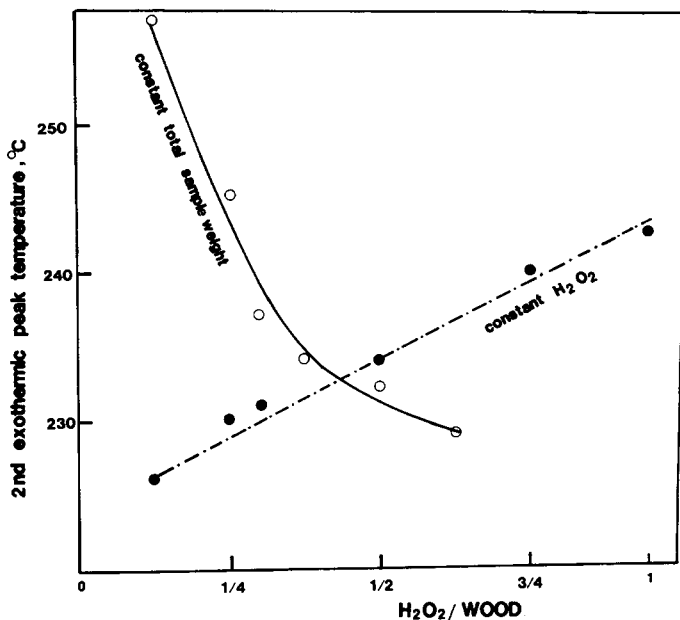


Fig. 15. Relationship between maximal peak temperature and H₂O₂/wood ratio. Second exothermic peak.

thermal behavior of the mixtures was observed. Both the first and second exothermal peaks were broader with the second exothermal peak overlapped by an endotherm [Fig. 11(b)]. In the case of the first exotherm, the peak height was a linear function, and the peak area an exponential function of the H₂O₂/wood ratio (Figs. 12 and 13). The temperature of the first exothermal peak increased with increasing H₂O₂/wood ratio between 1/8 and 3/8, and then remained relatively constant up to a ratio of 1. This is consistent with the work of Melling et al.⁸ and Barrall and Rogers,³ who showed that peak temperature is not a function of thermal conductivity, but rather increases slightly with increasing density and specific heat. Increasing the H₂O₂/wood ratio while keeping the total mixture weight constant increases the density and heat capacity of the mixture because the density and heat capacity of H₂O₂ (50% w/w) is about three to four times larger than that of oven-dried wood (H₂O₂ 50% w/w: density = 1.1914 g/cc at 25°C; heat capacity = 0.790 cal/g-soln-°C at 27°C⁹; oven-dried white fir: density = 0.38 g/cc; heat capacity = 0.257 cal/g-°C at 27°C).¹⁰

With mixtures prepared by method 2, the second exotherm, unlike the first exotherm, showed a decrease in peak temperature with an increasing H₂O₂/wood ratio, apparently due to the presence of higher O₂ concentrations at higher ratios. The second exotherm was broader at low H₂O₂ wood ratios and was overlapped by an endotherm at high ratios. This endotherm corresponds to water evaporation (water from 50% w/w H₂O₂ solution and from H₂O₂ decomposition).

The thermal properties of an exothermic process are determined not only by the thermal properties of the sample, but also by the thermal conductivity between the sample and sample holder and the sample holder and platform. Unlike endothermic processes, which always set up transition fronts, an exothermic reaction liberates heat which can cause the sample temperature to rise above that of the heating platform creating a gradient whereby heat can transfer

from the sample to the platform. With mixtures prepared by method 1, the same amount of H_2O_2 was distributed over a larger amount of wood as the H_2O_2 /wood ratio was decreased. Thus, at lower H_2O_2 /wood ratios, the heat transfer path was much less continuous and the amount of H_2O_2 (liquid) available at the surface was greatly reduced as compared with the higher H_2O_2 /wood ratios. At H_2O_2 /wood ratios below 1/2 this was evidenced by smaller peak heights, indicative of reduced reactivity. When the mixtures were prepared by method 2, the increased quantity of H_2O_2 at a constant total sample weight resulted in more continuous heat transfer and greater surface contact between the sample and the sample holder at higher H_2O_2 /wood ratios. This was evidenced by a linear increase in peak height with an increasing H_2O_2 /wood ratio.

It is important to note that the total heat of reaction was relatively constant for samples prepared by method 1, in which the same quantity of H_2O_2 was added per sample mixture, while the total heat of reaction increased for an H_2O_2 /wood ratio of 1/8 to 3/8 and then remained relatively constant for an H_2O_2 /wood ratio up to 1, when the mixtures were prepared by adding increasing quantities of H_2O_2 per total sample weight (Figs. 13–14). In the latter case, the reduced enthalpy values at lower H_2O_2 /wood ratios were partially the result of reduced heat capacity at lower H_2O_2 /wood ratios.

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