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DIFFERENTIAL SCANNING CALORIMETRY OF HYDROGEN PEROXIDE AND HYDROGEN PEROXIDE-TREATED LIGNOCELLULOSE. II. ANALYSIS AT ELEVATED PRESSURE *

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ABSTRACT

Behavior of aqueous hydrogen peroxide in the presence and in the absence of wood flour, cellulose, lignin, and arabinoxylan was examined by DSC in nitrogen atmosphere at various pressures up to 950 psi. Increased pressure effectively shifted the evaporation endotherms of water and hydrogen peroxide to higher temperatures and allowed examination of exotherms resulting from catalytic decomposition of hydrogen peroxide and oxidation by hydrogen peroxide of lignocellulosic materials. Treatment of alodined aluminum pans and soda glass pans with hot nitric acid and treatment of gold pans with aqueous sodium sulfide and hot hydrogen peroxide strongly reduced the catalytic effect of the pan surface on decomposition of hydrogen peroxide. Of the lignocellulosic materials tested, arabinoxylan proved to be most reactive in respect to hydrogen peroxide.

INTRODUCTION

The DSC results at ambient pressure [1] indicated that the exotherms for the decomposition of hydrogen peroxide and for the reaction between wood and hydrogen peroxide are partly overlapped by the endotherms due to evaporation of either hydrogen peroxide aqueous solutions or of water. This overlap occurred whether the sample was contained in an open pan or in a closed pan provided with a pin hole in the lid. This limited the studies of hydrogen peroxide decomposition and of the reactions between hydrogen peroxide and lignocellulose. A convenient way for alleviating this difficulty is to shift to higher temperatures the evaporation endotherms by increase of pressure. The relationship between temperature and equilibrium vapor pressure of the liquid is given by the familiar Clapeyron—Clausius equation

$$\ln\frac{P}{P_0}=\frac{\Delta H_v}{RT}+\frac{\Delta H_0}{RT_0}$$

where P_0 is the vapor pressure at temperature T_0, and P is the vapor pressure at T. The equation provides that changing the vapor pressure will cause a

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* This paper is taken, in part from the Ph.D. dissertation of Dr. Nguyen.

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shift in the boiling points of hydrogen peroxide or water and suggests the use of pressure cells where the pressure surrounding the sample could be varied over a wide range.

Thermal analysis under high pressure has been used for studying pressure-sensitive reactions, resolution of competitive reactions [2], evaluation of catalysts [3], deaquation reactions of metal salts [4], and thermodynamic changes and quantitative determinations at high pressure [5,6].

In this paper we are reporting on the chemical behavior of aqueous hydrogen peroxide in the presence and absence of lignocellulosic materials at pressures up to about 1000 psi, and are concurrently examining the effect of various treatments of the pans on surface catalysis of the hydrogen peroxide decomposition reaction.

MATERIALS AND METHODS

The high pressure DSC system with complete valving and connections has been described by Levy et al. [2]. The modified instrument used in this study consisted of a Du Pont Standard DSC cell enclosed in a steel pressure chamber capable of operating at a maximum pressure of 1000 psi or a vacuum of 10 μ. The operation was carried out by placing the sample and reference on their respective platforms and sealing the pressure chamber according to the manufacturer's directions. Pressurized N_2 gas was allowed to flow through partially open input and output valves for 5 min to displace the air in the pressure chamber. The output valve was then closed and the pressure was adjusted to a predetermined level by a regulator installed on the gas cylinder. The output valve was then opened again and the flow rate was controlled at 50 ml min^{-1}. Once the system pressure was stabilized, the heating cycle was started. Except for some small loss of sensitivity at high pressures due to the changes in heat transfer characteristics and the necessity to pres-

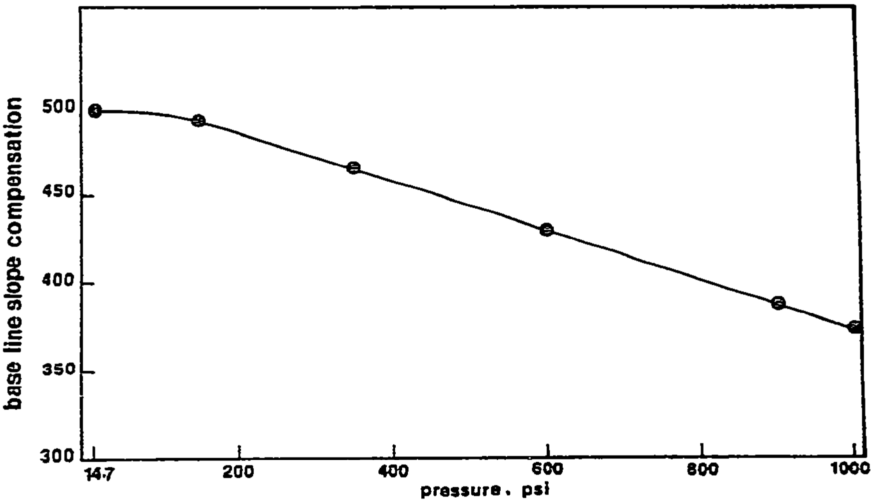

Fig. 1. Correlation between baseline slope compensation and pressure.

sure calibrate the slope compensation, the overall operation of the pressure DSC cell was quite similar to that of the standard DSC cell, and its performance was identical to that of the DSC cell at ambient pressure [2].

In order to obtain a horizontal baseline, the baseline slope compensation of the DSC cell base had to be calibrated with respect to pressure. The relationship between baseline slope compensation and pressure was determined experimentally and is shown in Fig. 1. There was little change in baseline slope compensation between ambient pressure and 125 psi. However, above 125 psi, the baseline slope compensation was an inverse linear function of pressure and followed the equation: $B = 0.0014P + 5.18$, where B is the baseline slope compensation and P is the pressure in psi.

Nitrogen gas was used throughout all measurements and the heating rate was 20°C min^{-1}, as before [1]. The pans used were either open or hermetically sealed and provided with a pin hole in the cover and were made of gold, alodined (pyrophosphate/fluoride treated) aluminum, pure aluminum, and soda glass. Hydrogen peroxide used was ACS reagent grade, 50 wt.% (Perone 50) *. The lignocellulosic materials used included (a) white fir wood [1]; (b) commerical Sigmacell Type 38 cellulose, made by Sigma Chemical Co.; (c) alkali insoluble arabinoxylan as hemicellulose [7]; and (d) powderized, sieved (<100 mesh), and extracted with 95% ethanol (12 h) and hot water (12 h) brown cubical rot from *Libocedrus decurrens* Torr. (produced by fungus *Polyporus amarus*) as a model for lignin; the material contained 10—15% carbohydrates according to Klason lignin determination. The DSC characteristics of this material did not differ from Björkman and Klason lignins, compared on the basis of the H_2O_2 oxidation reaction. To remove the catalytically acting heavy metal ions all lignocellulosic materials were treated with EDTA, as described elsewhere [1].

RESULTS AND DISCUSSION

DSC of hydrogen peroxide solution in different types of sample holders at higher pressure

The DSC curves of H_2O_2 in pinhole alodined aluminum pan at ambient, 300 and 950 psi pressures are shown in Fig. 2 and Table 1. As mentioned earlier [1], the alodine process activates the aluminum surface, which becomes catalytic for the decomposition of hydrogen peroxide at temperatures below 100°C. The DSC curves show an exotherm corresponding to the decomposition of H_2O_2 solution and the endotherms corresponding to the evaporation of water at corresponding pressures. The onset temperature of the endotherm obtained at 950 psi pressure (245°C) (boiling point) is somewhat lower than the value obtained from the steam table (281°C). Some increase in exothermic peak temperatures was observed when the pressure was increased from ambient to 950 psi, i.e., the pressure somewhat reduced

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* Courtesy of Du Pont Chemical Co.

TABLE 1

DSC characteristics of 50% wt. H_2O_2 and H_2O_2-treated wood at different conditions of sample holders and elevated pressures (Heating rate: 20°C min^{-1}; gas: N_2)

Sample-holder types and conditions	First exotherm (decompn. of H_2O_2 or decompn. and reaction of H_2O_2 and wood) peak temp. T_1 (°C)	Endotherm (evaporation of H_2O_2 or H_2O)
50% wt. aqueous H_2O_2		
Pinhole hermetic alodined aluminum pan		
(a) 300 psi	94	235 (H_2O)
(b) 950 psi	98	295 (H_2O)
Pinhole hermetic alodined aluminum pan treated with:		
(a) soaking in 50% H_2O_2 at 24°C for 2 h	116	
(b) as (a) but for 24 h	127	
(c) boiling in 50% H_2O_2 for 1/2 h	155	
(d) as (c) but for 3 h	165	
(e) boiling in 15% HNO_3 for 1/2 h, and in 50% H_2O_2 for 1 h	188.5	
Open soda glass pan at 800 psi, untreated	119	165 (H_2O)
Open soda glass pan at 800 psi, fused, soaked in 15% HNO_3 and boiled in 50% wt. H_2O_2		173 (H_2O_2)
Pinhole hermetic gold pan at 800 psi, untreated	88	262 (H_2O)
Pinhole hermetic gold pan at 800 psi, poisoned with Na_2S	140	256 (H_2O)
Pinhole hermetic plain aluminum pan at 975 psi	187	287.5 (H_2O)
Pinhole hermetic plain aluminum pan at 975 psi; 0.025% Fe^{2+} added to 50% wt. H_2O_2	62	
50% wt. H_2O_2-treated wood		
Pinhole hermetic alodined aluminum pan at 300 psi	135	232 (H_2O)
Pinhole hermetic alodined aluminum pan at 950 psi	172[a] (shoulder at 105)	
Pinhole hermetic plain aluminum pan at 975 psi	183[b]	

[a] Second exotherm at 220°C.

[b] Second exotherm at 236°C.

the catalytic effect of pan surface on the decomposition of aqueous hydrogen peroxide. This can be explained by an increase with pressure of the amount of gas adsorbed on the alodined surface reducing the diffusion rate of hydrogen peroxide to the vessel surface [11]. Roiter [8] similarly found that the rate of hydrogen peroxide decomposition on platinum foil is increased

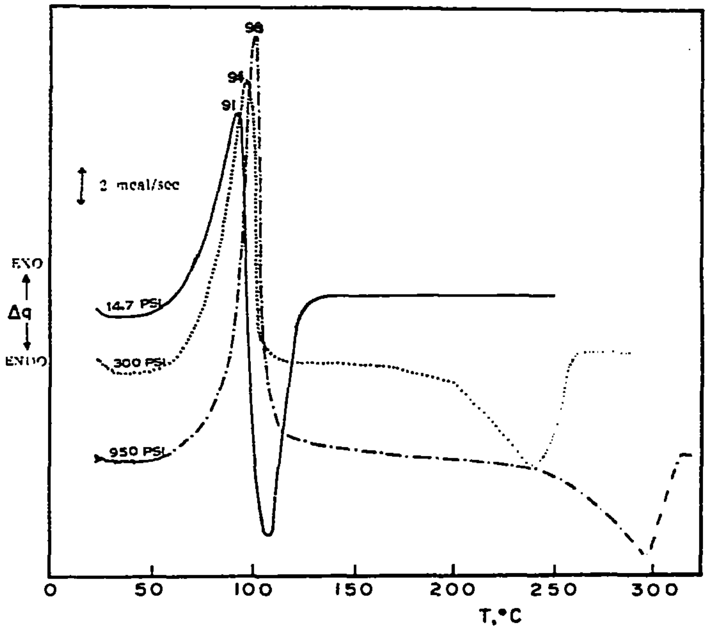

Fig. 2. DSC curves of 50% wt. H_2O_2 in pinhole alodined aluminum pan at different pressures. Heating rate: 20°C min^{-1}; atmosphere: N_2; sample size: ~3 mg.

by a reduction of pressure, presumably because the adsorbed gas was removed from the surface of the catalyst by pressure reduction.

When the alodined aluminum pans were subjected to various oxidative treatments, the exothermic peaks of H_2O_2 decomposition moved to higher temperatures (Fig. 3, Table 1). The treatments used were as follows:

(a) soaked in H_2O_2 at 24°C for 2 h, washed with distilled water, and dried;
(b) same as (a) but soaking continued for 24 h;
(c) soaked in boiling 50% H_2O_2 for 30 min, washed with boiling distilled water, and dried;
(d) as (c) but boiled for 3 h;
(e) soaked in boiling 15% HNO_3 for 30 min, then in boiling 50% H_2O_2 for 1 h, washed with boiling distilled water, and dried.

The results indicate that the catalytic effects of alodined pan on aqueous hydrogen peroxide decomposition could be strongly reduced by treatment with hot H_2O_2 solution or the combination of hot HNO_3 and H_2O_2, with the latter being more effective.

DSC curves for H_2O_2 in catalytically active hermetic gold pan run at 800 psi (Fig. 4a) followed the pattern that was observed for hermetic alodined aluminum pans. Soaking the gold pan for 15 min in a solution composed of one part Na_2S and 50 parts of water (adjusted to pH 8.0 with HCl) deactivated its surface considerably and raised the exothermic peak temperature from 89°C to 140°C, with the decomposition process taking place more slowly in the early stages (Fig. 4b). Another surface which often concerns the investigator interested in hydrogen peroxide decomposition is the glass commonly used for storing hydrogen peroxide solutions Giguère [9] reported that the temperature at which the rate constant for decomposition of the

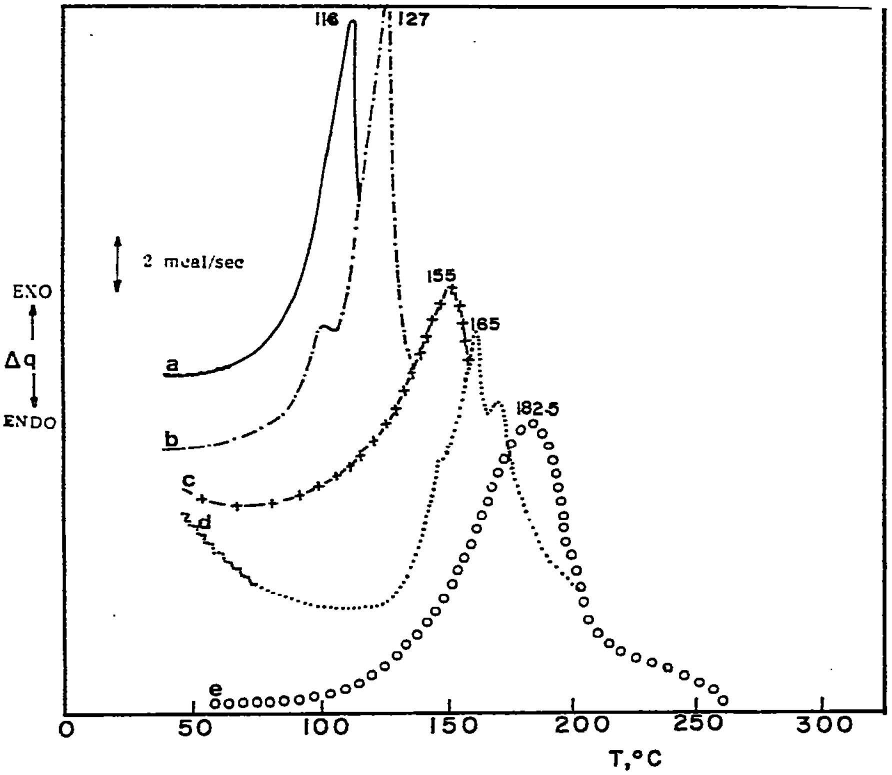

Fig. 3. DSC curves of 50% wt. H_2O_2 in pinhole alodined aluminum pan treated with various inactivating reagents. Heating rate: 20°C min^{-1}; atmosphere: N_2 at 800 psi; sample size: ~5.0 mg. a, Soaking in 50% wt. H_2O_2 at 25°C for 2 h; b, as (a) but for 24 h; c, boiling in 50% wt. H_2O_2 for 30 min; d, as (c) but for 3 h; e, boiling in 15% HNO_3 for 30 min and in 50% wt. H_2O_2 for 1 h.

vapor of hydrogen peroxide of 95% concentration equals 10^3 s^{-1} is 150°C for pyrex, 240°C for fused pyrex and 157°C for pyrex washed with hot water, but only 100°C for soda lime, 125°C for transparent silica and 150°C for fused transparent silica. Ivanov and Dochikjan [10] found that after 4 months of storage at room temperature the concentration of hydrogen peroxide decreased from an original 2.93% value to 0.02% in clear glass, to 0.48% in brown glass and to 2.71% in paraffin coated glass. The factors responsible for the heterogeneous decomposition of hydrogen peroxide under these storage conditions are most likely the alkaline nature of common glass aided by roughness and minute scratches of the inner walls of the container.

By design, the differential thermal sensors of a DSC cell are located externally to the sample holders. In such a situation, glass is not an ideal sample-holder material due to its low thermal conductivity. However, for the purpose of comparing the relative magnitude of the effects of different glass treatments on H_2O_2 decomposition, this is immaterial. The DSC curve of hydrogen peroxide solution in an open untreated glass container at 800 psi is shown in Fig. 5a (an empty glass container was used as the reference). The glass container was round, 4 mm in diameter and about 1 mm thick and flat at the bottom. When this glass container was washed with boiling water,

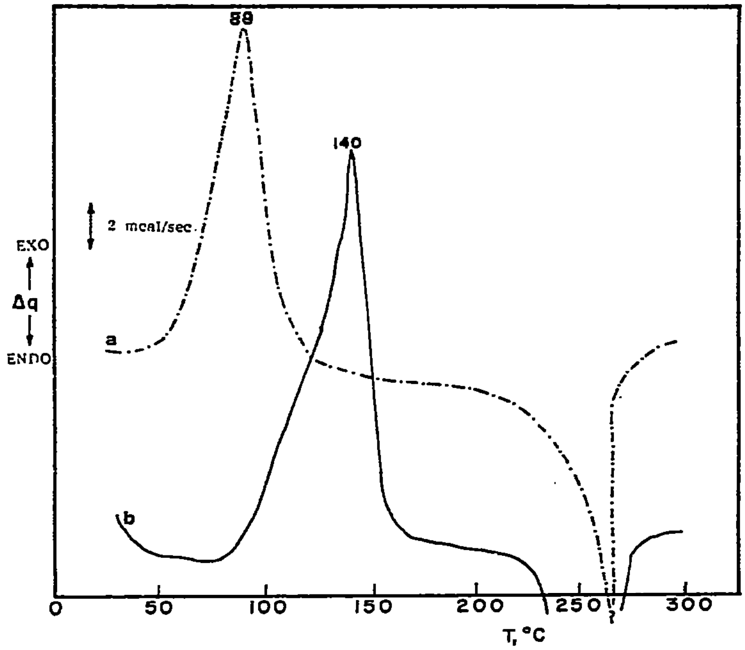

Fig. 4. DSC curves of 50% wt. H_2O_2 in gold pans. Heating rate: 20°C min^{-1}; atmosphere: N_2 at 800 psi; sample size: 4.2 mg. a, Pinhole gold pan, untreated; b, as (a) but treated with 2% Na_2S solution.

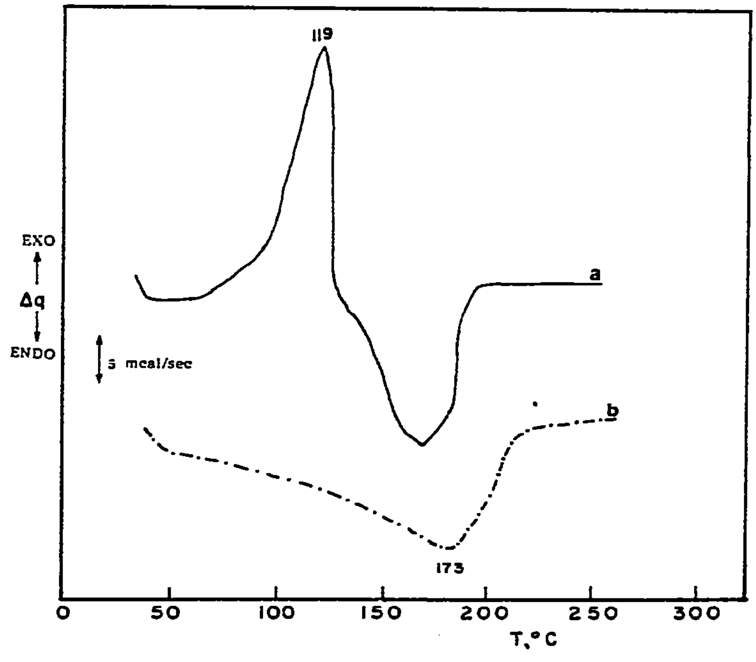

Fig. 5. DSC curves of 50% wt. H_2O_2 in open soda glass pans. Heating rate: 20°C min^{-1}; atmosphere: N_2 at 800 psi; sample size: ~7 mg. a, Common soda glass, untreated; b, as (a) but fused, soaked in 15% HNO_3 for 24 h at ambient temperature, and finally boiled in 50% wt. H_2O_2 for 30 min.

DSC patterns were similar to those of untreated gold or alodined aluminum pans, exhibiting an exotherm peaking at 119°C corresponding to catalytic hydrogen peroxide decomposition, followed by an endotherm corresponding to water evaporation. When the same container was fused, treated with 15% HNO_3 for 24 h at room temperature and finally soaked in boiling 50% H_2O_2 for 30 min, only one broad endotherm (Fig. 5b) corresponding to the evaporation of hydrogen peroxide was obtained. While this indicated that the glass surface could be deactivated to some extent, the experiments were not pursued any further due to unavailability of appropriate commercial glass sample holders and the mentioned poor thermal conductivity of glass.

DSC curves of hydrogen peroxide decomposition at 975 psi in pinhole plain aluminum pan, pretreated with boiling 15% HNO_3 and boiling 50% H_2O_2, are shown in Fig. 6. As indicated in Part I [1], in the case of plain aluminum pans this treatment did not have much effect on the thermal behavior of hydrogen peroxide solution, but it was felt necessary in order to produce consistently fresh sample-holder surfaces. The DSC curve shows an exothermal peak at 187°C corresponding to the decomposition of hydrogen peroxide solution, followed by an endotherm corresponding to the evaporation of water. This pattern was identical with that of hydrogen peroxide analyzed in pinhole alodined aluminum pan which was treated with

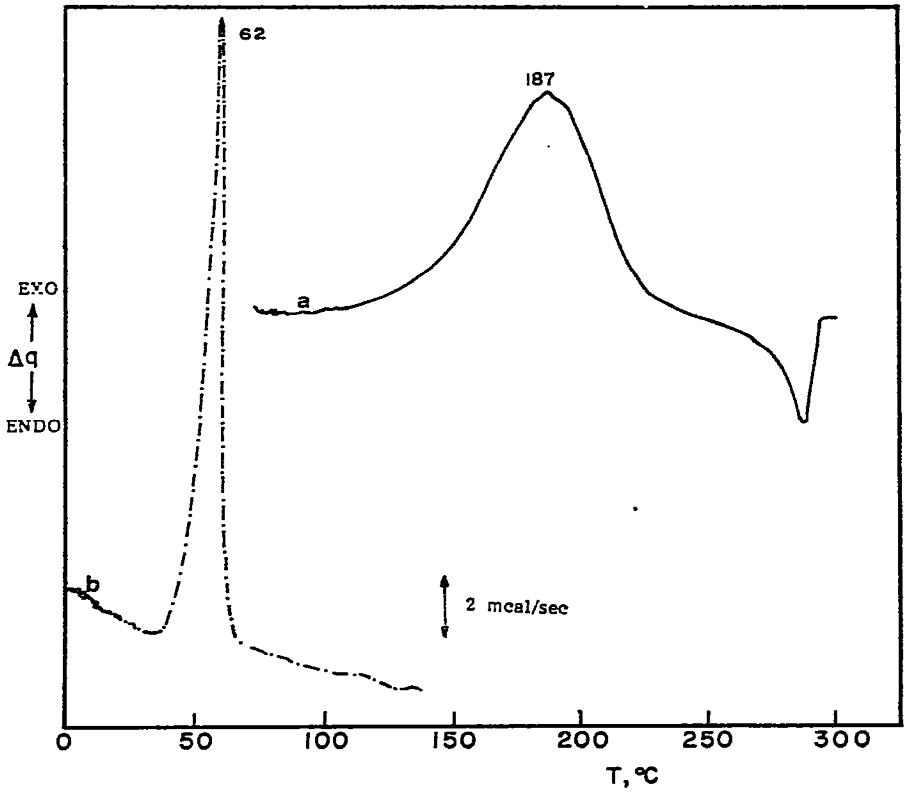

Fig. 6. DSC of 50% wt. H_2O_2. Heating rate: 20°C min^{-1}; atmosphere: N_2 at 975 psi; sample size: 1.78 mg. a, In pinhole plain aluminum pan; b, as (a) but with added 0.025% Fe^{2+}.

boiling HNO_3 followed by boiling H_2O_2, and indicates that HNO_3/H_2O_2 treatment completely deactivates the catalytic effect of pyrophosphate/fluoride treatment. From Fig. 6a it is evident that high pressures efficiently suppress the evaporation endotherm of hydrogen peroxide observed earlier [1] under ambient pressure conditions, and that the exothermic decomposition process of hydrogen peroxide can be efficiently observed for quantitative studies. It is not known whether or not there are any pressure effects on the reaction parameters of the exothermal decomposition of H_2O_2 solution of Fig. 6a. It was not possible to examine these types of effects for technical reasons — a decrease in pressure of appropriate magnitude would result in overlapping of the decomposition exotherm and the evaporation endotherm, while an increase in pressure above 1000 psi cannot be achieved with the Du Pont pressure DSC cell.

Differential scanning calorimetry can also be used to characterize the effect of added catalyst on the decomposition of hydrogen peroxide solution, as shown in Fig. 6b. The sample contained in a pinhole plain aluminum pan consisted of one part of ferrous ion ($Fe\ SO_4(NH_4)_2SO_4 \cdot 6H_2O$) to 4000 parts of 50 wt.% hydrogen peroxide solution. Both hydrogen peroxide and catalyst were kept at —5°C and were mixed in an ice bath. The DSC cell was cooled with liquid nitrogen to —30°C before placing the sample pan on the platform. As seen from the curve, catalysis by ferrous ion shifted the decomposition peak temperature of 50° H_2O_2 from 187°C to 62°C.

DSC of hydrogen peroxide-treated lignocellulose in different types of sample holders

DSC curves of hydrogen peroxide-treated wood flour run in a pinhole alodined aluminum pan at ambient, 300 and 950 psi are shown in Fig. 7. The results indicate that, although the reaction starts at about the same temperature for all pressures, the peak temperatures are markedly different and depend upon pressure — the lower the pressure, the earlier the peak occurred. At 950 psi the exothermic peak temperature was 172°C, approximating the exothermic peak temperature of 50% H_2O_2-treated wood run in a plain, rather than in an alodined pinhole aluminum pan. The differences in shape exhibited by the exotherms at different pressures and the appearance of a second exothermic peak at 950 psi pressure suggest that different mechanisms of hydrogen peroxide decomposition and hydrogen peroxide oxidation of lignocellulosic materials may function at different pressures. At low pressures both reactions are predominantly controlled by the catalyst, while at elevated pressures the reactions are initiated only by the catalyst, whereas maximum reaction rates are controlled by temperature. This behavior is markedly different from that of hydrogen peroxide run in the absence of wood flour (Fig. 2). The reasons for such differences and the strong effect of pressure on the reaction between lignocellulose and hydrogen peroxide are not known. DSC results for hydrogen peroxide solution and hydrogen peroxide-treated lignocellulose run under various treatment conditions and pressures and in various sample holders are summarized in Table 1.

Figure 8 shows the DSC curves of hydrogen peroxide treated cellulose (a),

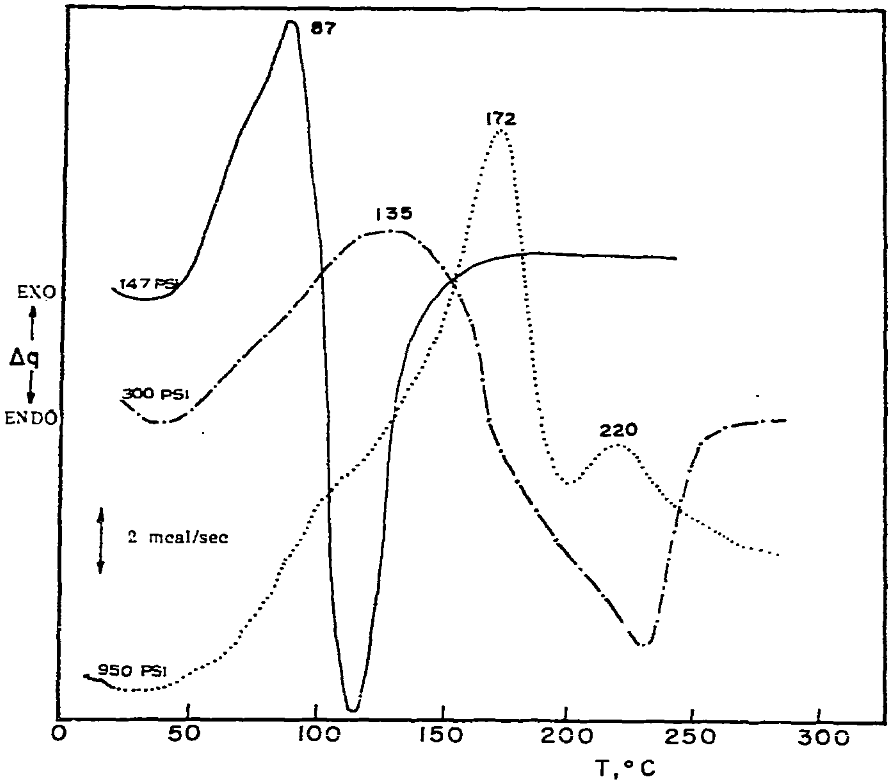

Fig. 7. DSC curves of 50% wt. H_2O_2-treated wood at different pressures in pinhole alodined aluminum pans. Heating rate: 20°C min^{-1}; atmosphere: N_2; sample size: 1.42 mg.

lignin (b), wood (c) and hemicellulose (arabinoxylan) (d). The samples were run at a N_2 pressure of 975 psi in a pinhole plain aluminum pan pretreated with boiling 15% HNO_3 and boiling H_2O_2. Hydrogen peroxide-treated lignocellulosic materials generally undergo two exothermic processes which differ in extent and peak reaction temperatures (T_1 and T_2) and depend on the nature of the lignocellulosic component. The results show that H_2O_2 is more reactive toward lignin than toward cellulose with the H_2O_2—lignin reaction rate being higher, as indicated by the sharper peak. Compared to lignin, the second exothermic peak is significant in cellulose, whereas practically no second exothermic reaction is seen in the DSC curve for the H_2O_2—lignin reaction. The DSC curve of wood treated with hydrogen peroxide is very similar to that for cellulose, although the peak temperature (T_2) and heat of reaction (peak area) of the second exotherm are smaller for H_2O_2-treated wood than for H_2O_2-treated cellulose. Compared to wood and cellulose, hemicellulose is much more reactive toward hydrogen peroxide, exhibiting a much higher reaction rate. With hemicellulose the second exothermic process occurs at a lower temperature and generates greater heat than does the second exothermic reaction for either cellulose or wood. Rigorous examination of the two peaks will be the subject of study and discussion in subsequent papers.

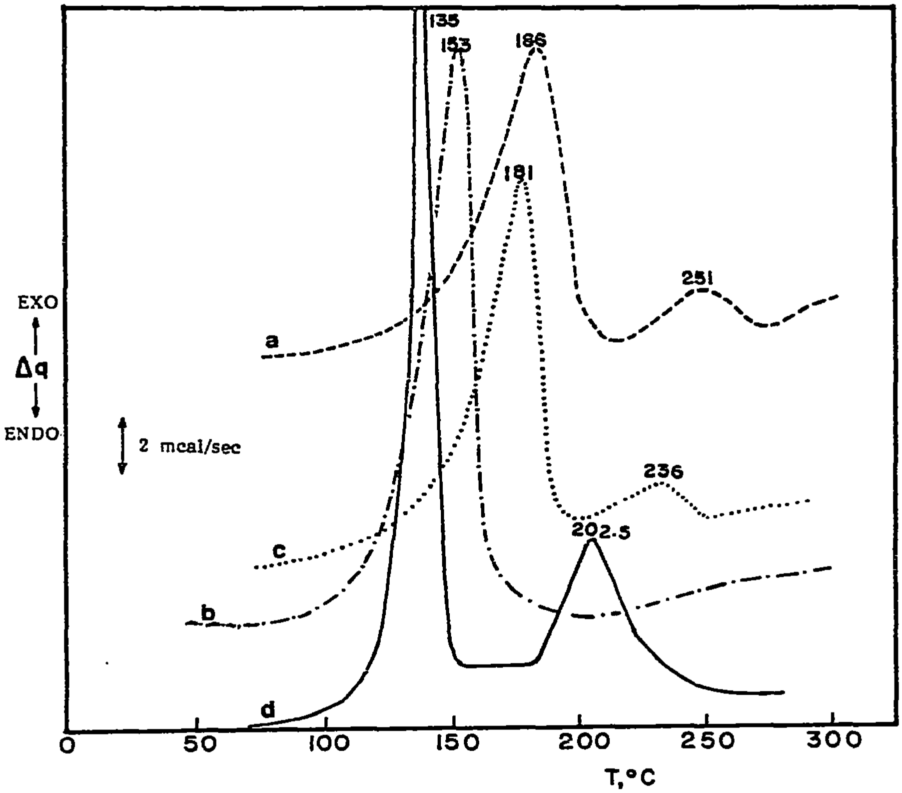

Fig. 8. DSC curves of 50% wt. H_2O_2-treated lignocellulosic materials in pinhole plain aluminum pans. Heating rate: 20°C min^{-1}; atmosphere: N_2 at 975 psi; sample size: 1.42 mg. a, Cellulose; b, brown rot lignin; c, wood; d, arabinoxylan.

CONCLUSIONS

The optimal procedure for studying the decomposition and oxidation of lignocellulosic materials by hydrogen peroxide includes (a) use of cells allowing runs under increased atmospheric pressure, such as 950 psi, and (b) use of hermetically sealed pans provided with a pin hole in the cover, made from pure aluminum and pretreated by boiling in 15% nitric acid for 30 min and 50 wt.% hydrogen peroxide for 60 min. The pressure provides the separation of evaporation endotherms from reaction exotherms by shifting the former to higher temperatures, while the oxidative treatments provide the catalytically least active pan material.

Carbohydrate components of wood, i.e., cellulose and hemicelluloses, show two oxidation exotherms with hydrogen peroxide, one below 200°C and the other above 200°C, while lignin exhibits a single exotherm peaking at 153°C. Of the compounds studied, the hemicellulosic arabinoxylan appeared to be the most reactive and cellulose the least reactive.

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