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THERMAL ANALYSIS OF MIXTURES OF NITRATES AND LIGNOCELLULOSIC MATERIALS

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ABSTRACT

The reactions between 20 different inorganic nitrates and wood flour, microcrystalline cellulose, precipitated cellulose, preparations of soft- and hardwood lignin, and xylan have been studied by DSC, TG, DTG, and infrared spectroscopy. In DSC (800 psig, in N_2) the exotherm arising from the oxidation of lignocellulosic materials by nitrates appeared between 150 and 200°C; in the majority of cases these values were only transgressed with the most and least acidic nitrates. Positive correlations of < 0.01 significance were obtained between the peak temperature of the oxidation exotherms and pH of the 1 N solutions of nitrates. After the oxidation reaction the acidity of the lignocellulose/nitrate mixtures decreased in all cases with the exception of ammonium and silver nitrates. The increase in acidity in the last two cases was explained by the oxidation and/or volatilization of the ammonium ion and by the reduction of Ag^+ to metallic silver by lignocelluloses, respectively. Softwood lignin gave overall higher heats of reaction than carbohydrates. At higher pH values the heats of reaction tended to decrease, probably due to incomplete usage of the nitrate. A weak negative correlation was obtained between the activation energies and reaction rate constants and pH of the oxidation products. In TG the temperature of the maximum rate of weight loss decreased as the acidity of the nitrates increased. The infrared analysis of the oxidized products indicated the formation of the salts of carboxylic acids, rather than of esters as was the case with the nitric acid oxidations.

INTRODUCTION

The present investigation represents the continuation of our efforts to shed light on the mechanism of wood bonding by oxidative activation of the wood surfaces [1]. The wood bonding methodology involved employment of hydrogen peroxide/Fe^{2+} or nitric acid as oxidants with or without the use of crosslinking agents and resulted in particleboard exhibiting exceptional dimensional stability. In the previous paper we reported a thermoanalytical study of the interactions of nitric acid with various lignocellulosic materials

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under conditions simulating those used in the formation of composite products [2].

The present report includes thermoanalytical work on the reactions of various lignocellulosic materials with about 20 metal nitrates. It was hoped that the use of nitrates instead of nitric acid will result in products of higher pH, subject to reduced acid hydrolytical degradation and will provide additional control of the bonding process by inclusion of the pH variable.

EXPERIMENTAL

Reagent grade Li^+, Na^+, K^+, NH_4^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Al^{3+}, Pb^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Ag^+, Mn^{2+}, and Cr^{3+} nitrates were used without further purification. The preparation or sources of extractive-free white fir wood flour [(*Abies concolor*) (Gord. & Glend.) Lindl.] of 60/80 mesh, of microcrystalline and of precipitated cellulose, of xylan, of softwood brown-rot lignin from Incense-cedar (*Libocedrus decurrens* Torr.) with 90.4% Klason lignin content, and of hardwood brown-rot lignin from balsam poplar (*Populus balsamifera* L.) with 77.8% Klason lignin content have been described previously [2,3]. The procedures used in sample preparation, differential scanning calorimetric, thermogravimetric, and infrared analysis, and measurement of pH and nitrate contents of the samples were also described previously [2].

RESULTS AND DISCUSSION

DSC analysis

DSC tracings for lignocellulosic materials containing various nitrates are given in Figs. 1–6. The incorporation of nitrates produced a well-defined, moderately broad, new exothermic peak mostly below, and only occasionally not too far above 200°C, resulting from the oxidation of lignocelluloses by nitrates. Although oxidation by nitrates could follow a number of pathways [4] the most likely overall mechanism should involve the decomposition of nitrates into NO_2, O_2 and metal oxide with NO_2 oxidizing lignocelluloses under formation of NO. Oxygen should be partially used for reoxidation of NO to NO_2 and partially for direct oxidation of lignocellulose at appreciably higher temperatures (reactions 1–3):

$$Zn(NO_3)_2 \xrightarrow{\Delta} 2\ NO_2 + \tfrac{1}{2}O_2 + ZnO \tag{1}$$

$$NO_2 + \text{lignocellulosics} \rightarrow NO + \text{oxidized lignocellulosics} \tag{2}$$

$$NO + \tfrac{1}{2}O_2 \rightarrow NO_2 \tag{3}$$

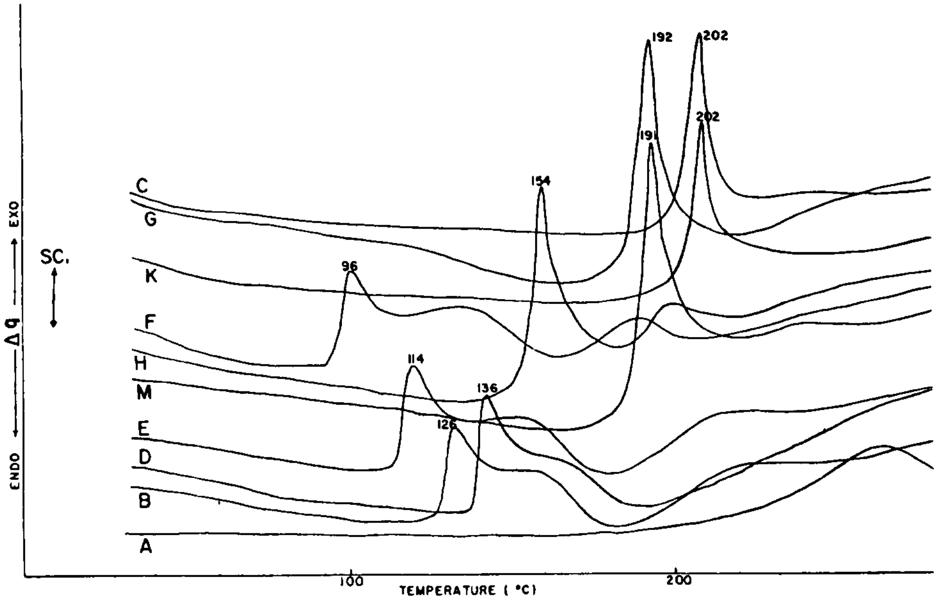


Fig. 1. DSC curves for wood flour treated with various nitrates; 20°C min^{-1} at 800 psig in N_2. Ordinate scale, SC = 2 mcal s^{-1}. (A) Not treated; (B) treated with $Al(NO_3)_3$; (C) treated with NH_4NO_3; (D) treated with $Be(NO_3)_2$; (E) treated with $Cr(NO_3)_3$; (F) treated with $Fe(NO_3)_3$; (G) treated with $Zn(NO_3)_2$; (H) treated with $Cu(NO_3)_2$; (J) treated with $Ca(NO_3)_2$; (K) treated with $Pb(NO_3)_2$; (M) treated with $Co(NO_3)_2$.

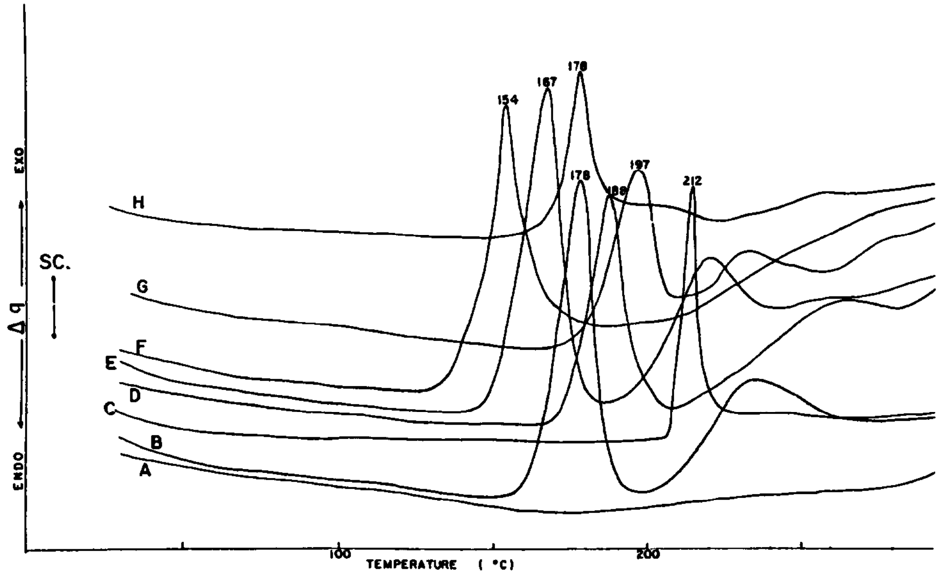


Fig. 2. DSC curves for microcrystalline cellulose treated with various nitrates. Conditions and symbols as in Fig. 1.

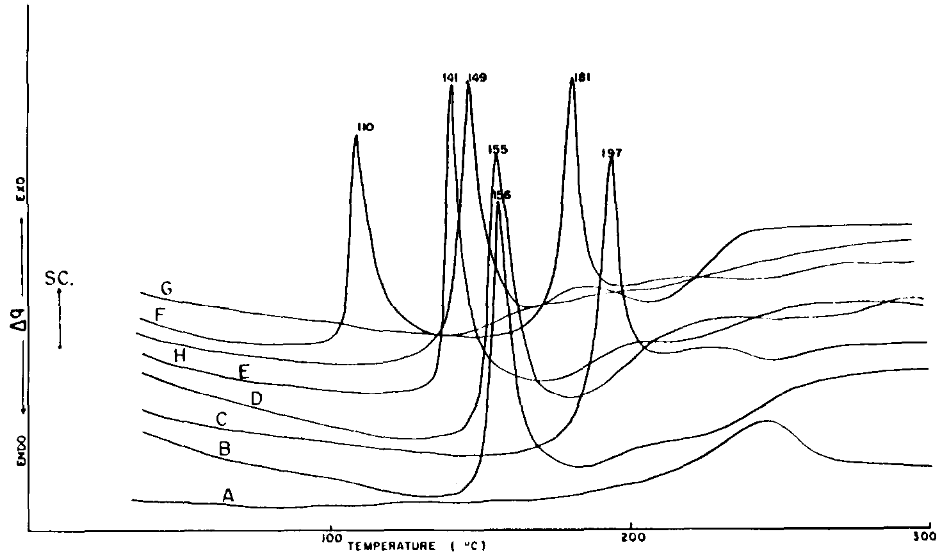


Fig. 3. DSC curves for brown-rot softwood lignin treated with various nitrates. Conditions and symbols as in Fig. 1.

Several nitrates behaved abnormally, however. Thus, lead nitrate reacted with microcrystalline cellulose to give three peaks. These three peaks could relate to the stepwise decomposition of lead nitrate to 4 PbO · 2 $Pb(NO_3)_2$, 5 PbO · $Pb(NO_3)_2$, and PbO under evolution of N_2O_5 in accordance with the

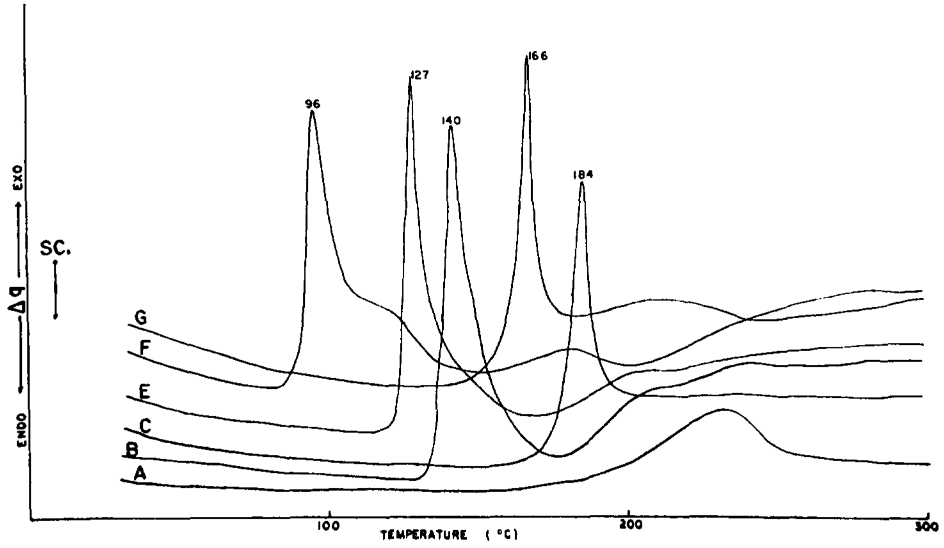


Fig. 4. DSC curves for brown-rot hardwood lignin treated with various nitrates. Conditions and symbols as in Fig. 1.

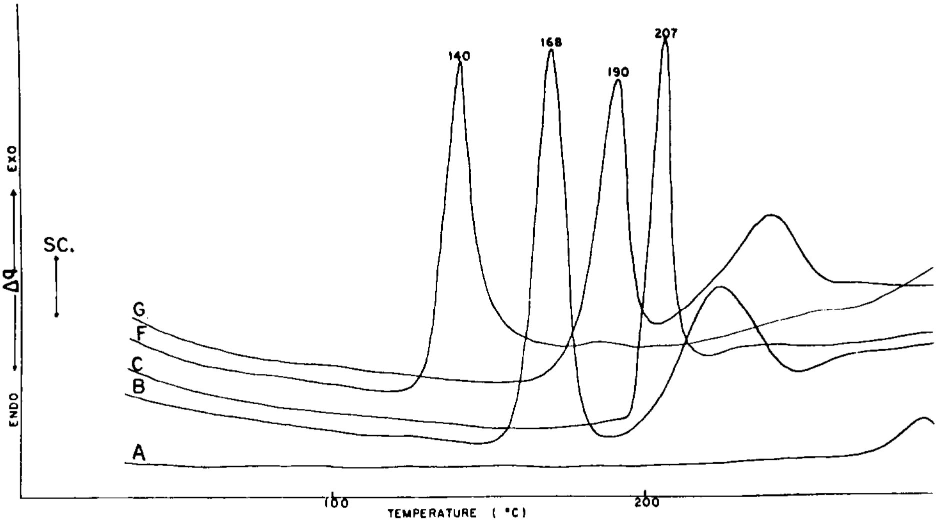


Fig. 5. DSC curves for precipitated cellulose treated with various nitrates. Conditions and symbols as in Fig. 1.

work of Neumann and Sonntag [5]. Silver nitrate reacted with lignocelluloses generally very vigorously, particularly in the case of lignins, producing an exceptionally thin and tall band; ammonium nitrate behaved similarly. The reasons for this will be discussed later.

The identification of the low-temperature exotherms with the oxidation of lignocellulosic materials by nitrates rather than with the oxidation-indepen-

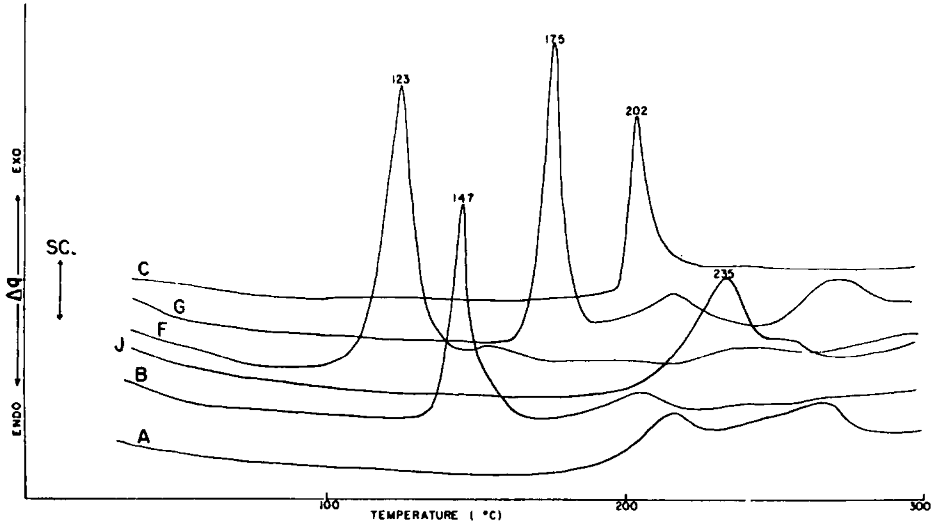


Fig. 6. DSC curves for xylan treated with various nitrates. Conditions and symbols as in Fig. 1, except that SC = 5 mcal s^{-1}.

dent decomposition of the nitrates is corroborated by the results of Gordon and Campbell [6] as well as by our DSC experiments run in the absence of lignocelluloses on about 20 nitrates used in this study. Gordon and Campbell reported DTA studies of 17 nitrates; the thermograms were dominated by endotherms in the lower temperature region. Exotherms appeared above 340 °C with the exception of ammonium nitrate with an exotherm peaking at 285 °C, and were poorly defined. Our experiments gave similar results with some nitrates producing no exotherms and some producing exotherms an order of magnitude weaker and at much higher temperatures than in the case of mixtures of nitrate and lignocelluloses. Our results are also in agreement with those of Miller [7] who studied the effect of zinc nitrate on the thermal behavior of cotton and found that exotherms obtained on cotton–nitrate mixtures did not correspond temperature-wise with the decomposition temperature of the nitrate alone. Based on this and other data Miller suggested that the exotherms obtained resulted from the oxidative attack of NO_2 on cellulose, NO_2 being produced by the thermal breakdown of the nitrate at relatively low temperatures. The lower breakdown temperature in the presence of lignocelluloses could relate to the existence of nitrate as an adsorbate on the lignocellulosic surface with the surface configuration of nitrate being quite different from that present in solution or in salts, and involving considerable enthalpy and entropy differences. It is also likely that the interaction of the polar groups on the surface of lignocelluloses with the cations of the salts (complexing, chelation) would produce a downward shift in the surface pH, i.e. result in a partial hydrolysis of the salts under formation of nitric acid [8]; this should facilitate decomposition to NO_2 as will be discussed later. Our results are also in accordance with the experiments of Karavaev and Kirillov [9] who determined temperatures of maximal release of nitric acid during thermal decomposition of nitrates; such temperatures did not correspond to the exothermic peak temperatures we observed on mixtures of nitrates and lignocelluloses.

The relation between the pH of nitrate solutions and the first exothermic peak temperatures

The data presented in Table 1 indicate that the first exothermic peak temperature of the nitrate–lignocellulose mixtures decreases as the acidity of the nitrate increases. When the temperatures for the first exothermic peak were plotted against pH values of the corresponding 1 N nitrate solutions, a linear relationship was observed (Fig. 7). The coefficients of determination (r^2) were high enough to be considered significant on a 0.01 level. The statistical data are summarized in Table 2. Attempts to correlate peak temperatures with pH values determined directly on treated samples instead of on 1 N nitrate solutions resulted in appreciably inferior correlations. This

TABLE 1

DSC data for the reaction between lignocellulosics and the various nitrates [a]

Nitrate	pH of 1 N solution	Wood flour		Microcrystalline cellulose		Precipitated cellulose		Softwood brown-rot lignin		Hardwood brown-rot lignin		Xylan	
		T (°C)	ΔH (kcal g^{-1})	T (°C)	ΔH (kcal g^{-1})	T (°C)	ΔH (kcal g^{-1})	T (°C)	ΔH (kcal g^{-1})	T (°C)	ΔH (kcal g^{-1})	T (°C)	ΔH (kcal g^{-1})
Al^{3+}	2.24	126	0.998	178	1.202	168	1.226	156	1.729	140	1.076	147	1.306
NH_4^+	4.72	202	1.241	212	0.920	207	1.072	197	1.241	184	0.818	202	1.321
Ba^{2+}	6.36	245		248				229		219			
Be^{2+}	1.58	136	1.220	188	1.195			115	3.314	135	1.658		
Cd^{2+}	4.04	203	1.251	201	0.367			190	1.148	169	0.863		
Ca^{2+}	5.13	217		247		233		211		191		232	
Cr^{3+}	1.63	114	0.993	167	1.500	155	1.978	141	3.091	127	1.468		
Co^{2+}	4.66	191	1.532	192	0.316			182	1.744	166	1.072		
Cu^{2+}	3.26	154	1.468	178	1.512			149	2.002	142	0.991		
Fe^{3+}	1.11	96	0.904	154	1.160	140	1.111	110	2.444	96	1.073	123	0.904
Pb^{2+}	3.45	202	1.032	[b]		204	0.713	193		180	1.584	207	0.422
Li^+	5.92	225		245				217		199			
Mg^{2+}	4.61	200	0.783	215	0.434			192	1.099	170	0.577	190	0.155
Mn^{2+}	3.84	196	1.257	181	0.838	208	0.467	192	1.772	169	0.661		
Ni^{2+}	3.94	193	1.153	204	0.784			182	1.840	166	1.280		
K^+	6.25	262		272				232		230			
Ag^+	3.99	177	1.474	215	1.421			162	1.343	136	1.525		
Na^+	6.52	260		276				230		212			
Sr^{2+}	5.69	221		260				211		193			
Zn^{2+}	4.11	192	1.879	197	0.823	190	0.765	181	2.502	166	0.717	175	0.906

[a] 800 psig, N_2, 20°C min^{-1}. T, peak temperature (°C) of the oxidation exotherm. Heat of reaction, ΔH (kcal g^{-1}), expressed in grams of NO_3^-.

[b] Peaks at 185, 199 and 212°C.

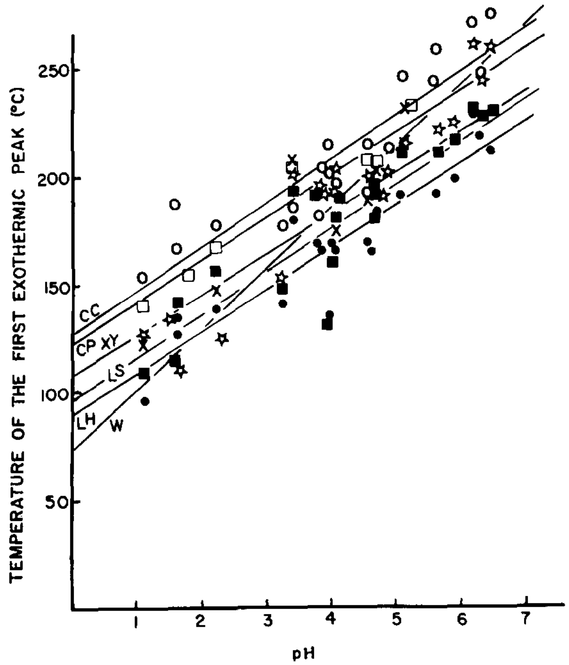


Fig. 7. Relationship between the temperatures of the first exothermic peak and pH values of 1 N nitrate solutions used for treatment of wood flour (W, ☆), microcrystalline cellulose (CC, ○), softwood brown-rot lignin (LS, ■), hardwood brown-rot lignin (LH, ●), precipitated cellulose (CP, □), and xylan (XY, ×).

suggests that some interactions between nitrates and lignocelluloses take place even at ambient temperature.

Not much could be gleaned from the literature with respect to the relationship between pH and the temperature of the first exothermic peak. A

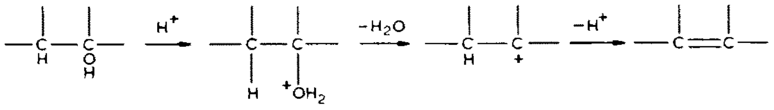
TABLE 2

Regression and correlation statistics for the relationship between temperature of the first exothermal peak (T_1) and pH [a]

Lignocellulosic material	Intercept *A*	Slope *B*	Confidence interval on slope	Coefficient of determination (r^2)	*df*
Wood flour	77.6	27.2	±3.89	0.923	18
Microcrystalline cellulose	127.4	20.1	±4.70	0.817	18
Brown-rot lignin of softwood	108.2	18.7	±3.42	0.880	18
Brown-rot lignin of hardwood	89.2	19.3	±3.84	0.861	18
Precipitated cellulose	122.2	19.5	±5.88	0.917	6
Xylan	99.9	22.7	±13.02	0.801	5

[a] Regression for $T_1 = A + B$ pH. For significance level of 0.01: $df = 18$, $r^2 = 0.315$; $df = 6$, $r^2 = 0.696$; $df = 5$, $r^2 = 0.794$.

positive rank correlation between pH and the endothermic peak temperature of the thermal decomposition of various paper materials was observed by Hebert et al. [10] but was not further discussed. Arseneau and Stanwick [11] studied by DSC and TG the thermal decomposition of cellulose in the presence of potassium chloride. They found that activation energies were a function of the square root of the ionic strength of the salt and suggested that one route of the thermal decomposition of cellulose was its dehydration through a carbonium ion (reaction 4):



$$-\underset{H}{\overset{|}{C}}-\underset{OH}{\overset{|}{C}}- \xrightarrow{H^+} -\underset{H}{\overset{|}{C}}-\underset{^+OH_2}{\overset{|}{C}}- \xrightarrow{-H_2O} -\underset{H}{\overset{|}{C}}-\overset{|}{\underset{+}{C}}- \xrightarrow{-H^+} -\overset{|}{C}=\overset{|}{C}- \qquad (4)$$

According to the authors anything that could stabilize the formation of carbonium ions would speed up the reaction. Thus a polar or an ionic environment should accelerate the reaction and thus decrease the peak temperature by contributing towards stabilization of the carbonium ion intermediate. It cannot be excluded that stabilization of the carbonium ions by the acid could also play a major role in the mechanism of the oxidation of lignocellulosic materials by nitrogen dioxide.

Another explanation for the effect of pH can be found in the mechanism of the thermal decomposition of nitrates. According to Duke et al. [12–14], the decomposition of nitrates proceeds through the nitronium ion, NO_2^+, which reacts with nitrate under eventual formation of NO_2 and O_2. Increase in acidity should result in an increase in concentration of nitronium ion and thus in the rate of NO_2 evolution. According to Levitt and Malinowski [15] and Hoggett et al. [16] the oxidizing (or nitrating) power of nitric acid depends upon its acidity, i.e. upon the rate of formation of NO_2^+. Topol et al. [17] could not confirm the presence of the nitronium ion in molten alkali nitrates, however, and found only a species similar to the dissolved NO_2. While proposing a mechanism which excluded the presence of NO_2^+ they indicated, nevertheless, that the rate of evolution of gaseous products should follow the acidic strength of the decomposing nitrates.

Variations in the acidity of the oxidized products

With most nitrates the acidity of lignocelluloses decreased after the first exotherm (Table 3). This drop in acidity should result from the formation of the metal salts of the weaker organic acids at the expense of salts of the strong nitric acid, used up during oxidation.

The oxidation reactions with ammonium and silver nitrates resulted, however, in products of increased acidity; both compounds also produced exceptionally tall and narrow exotherms in DSC. It is well known that the pyrolytic decomposition of ammonium nitrate leads predominantly to N_2O (reaction 5). While it cannot be excluded that in the presence of lignocellulo-

TABLE 3

Changes in pH of nitrate-treated lignocellulosics after the first exotherm

Nitrate	pH of 1 N solution	Change in pH of					
		Wood flour	Microcrystalline cellulose	Precipitated cellulose	Softwood brown-rot lignin	Hardwood brown-rot lignin	Xylan
Al^{3+}	2.24	0.68	0.37	0.51	1.07	1.15	0.68
NH_4^+	4.72	−1.28	−1.10	−0.82	0.14	−0.65	−1.43
Be^{2+}	1.58	1.44	1.43		1.01	1.44	
Ca^{2+}	5.13	1.21	2.31		0.79	1.77	
Cr^{3+}	1.63	1.47	0.59		1.22	1.30	
Co^{2+}	4.66	2.89	3.88		1.45	2.01	
Cu^{2+}	3.26	0.18	0.12		0.43	1.12	
Fe^{3+}	1.11	1.56	2.29	1.15	1.13	1.47	1.27
Pb^{2+}	3.45	0.92	1.95	0.03	1.30	1.31	−0.20
Li^+	5.92	1.53	2.57		3.08	2.17	
Mg^{2+}	4.61	4.58	3.03	2.46	2.37	3.46	3.85
Mn^{2+}	3.84	2.31	2.14		1.46	2.32	
Ni^{2+}	3.94	3.02	3.29		0.78	1.79	
Zn^{2+}	4.11	2.52	2.26	1.55	1.32	1.71	0.27
Ag^+	4.12	−0.62	−0.90		−1.87	−1.83	

ses the pyrolytic decomposition of ammonium nitrate could assume a different pathway, the increase in acidity (Table 3) during the reaction suggests the loss of NH_4^+ either by oxidation or by volatilization. The increase in acidity with silver nitrate suggests the oxidation of lignocellulosic materials by nitrate as well as by Ag^+ to metallic silver under liberation of the acids. It seems likely that the observed narrowness of the exotherms results from the increase in acidity during the reaction which should, in turn, progressively increase the acid catalysis of the oxidation reaction.

$$NH_4NO_3 \xrightarrow{\Delta} N_2O + 2\,H_2O \qquad (5)$$

Taking the pH of 3.5 of redwood heartwood [(*Sequoia sempervirens* (D. Don.) Endl.] (one of the most acidic woods) as the acceptable pH limit, the pH data obtained on lignocellulosic materials after the first exotherm indicated that with NH_4^+ (pH 2.73–3.47), Cr^{3+} (pH 2.89–3.37), and in some cases with Fe^{3+} (pH 3.04–4.41), Al^{3+} (pH 3.30–4.03), Ag^+ (pH 3.22–4.04) and Cu^{2+} (pH 3.16–4.50) nitrates this value was transgressed, i.e. that the use of these salts might result in weakening of wood by the acidic hydrolysis of cellulose.

Heats of reaction

Softwood lignin gave overall higher heats of reaction than carbohydrates ($\Delta \overline{H} = 2.169$, SD = 0.369 and $\Delta \overline{H} = 1.092$, SD = 0.237, respectively) (Table

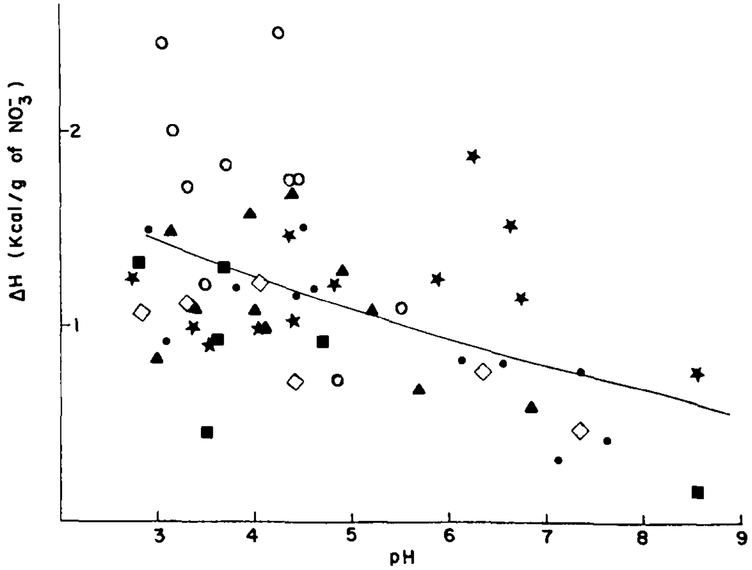


Fig. 8. Relationship between the heat of reaction (ΔH) and pH of the samples after completion of the first exothermic reaction. Wood flour (★) microcrystalline cellulose (●), softwood brown rot lignin (○), hardwood brown-rot lignin (▲), precipitated cellulose (□), and xylan (■).

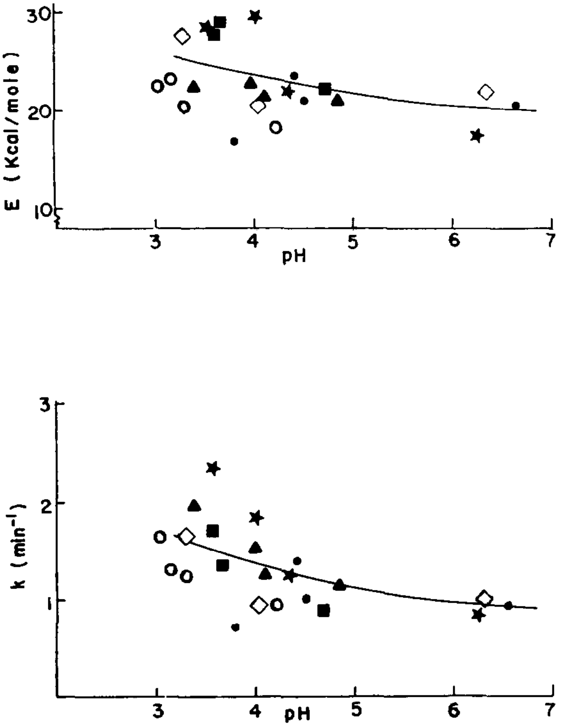


Fig. 9. Relationship between activation energy, E, and pH (above) and relationship between reaction rate constant, k, and pH (below). pH was measured on samples after completion of the first exothermic reaction. Symbols as in Fig. 8.

3). The heats of reaction of the hardwood lignin were, however, more in line with carbohydrates than with softwood lignin, most likely due to the 32% content of carbohydrates of the hardwood lignin preparation used. The temperature of the first exothermic peak was appreciably lower in precipitated cellulose than in microcrystalline cellulose, suggesting that accessibility plays an important role. The plot of the heat of reaction vs. pH value of the reaction product determined after the first exotherm gave the curve of Fig. 8. Between pH 1 and 5.5 the heat of reaction was largely independent of pH; the moderate fluctuations in the data are understandable in view of the heterogeneity of the lignocellulosic materials and variations in other experimental parameters. Above pH 5.5 the heat of reaction became gradually but

TABLE 4

Kinetic parameters for the first exothermic peak of lignocellulosic materials treated with various nitrates [a]

Material	Nitrate	pH of lignocellulosics		Activation energy, E (kcal mol^{-1})	Frequency factor, A (min^{-1})	Rate constant, k (min^{-1})
		Before run	After run			
Wood flour	Al^{3+}	3.34	4.02	30.01	4.95×10^{16}	1.853
	Zn^{2+}	3.72	6.24	17.66	1.76×10^{8}	0.875
	Fe^{3+}	2.00	3.56	28.64	2.23×10^{17}	2.368
	Cu^{2+}	4.18	4.36	22.10	2.51×10^{11}	1.238
Microcrystalline cellulose	Al^{3+}	3.43	3.80	16.94	1.16×10^{8}	0.719
	Zn^{2+}	4.31	6.57	20.73	4.04×10^{9}	0.938
	Fe^{3+}	2.12	4.41	23.60	1.65×10^{12}	1.397
	Cu^{2+}	4.38	4.50	21.10	1.66×10^{10}	0.999
Precipitated cellulose	Al^{3+}	3.52	4.03	20.93	2.18×10^{10}	0.940
	Zn^{2+}	4.78	6.33	22.16	2.86×10^{10}	0.998
	Fe^{3+}	2.15	3.30	27.88	9.06×10^{14}	1.627
Brown-rot lignin of softwood	Al^{3+}	2.23	3.30	20.51	3.43×10^{10}	1.233
	Zn^{2+}	2.90	4.22	18.58	8.49×10^{8}	0.953
	Fe^{3+}	1.91	3.04	22.80	1.33×10^{13}	1.667
	Cu^{2+}	2.73	3.16	23.31	1.51×10^{12}	1.291
Brown-rot lignin of hardwood	Al^{3+}	2.83	3.98	22.92	2.02×10^{12}	1.512
	Zn^{2+}	3.14	4.85	21.04	3.56×10^{10}	1.175
	Fe^{3+}	1.92	3.39	22.74	5.88×10^{13}	1.945
	Cu^{2+}	2.98	4.10	21.64	3.03×10^{11}	1.229
Xylan	Al^{3+}	2.99	3.67	28.81	1.33×10^{15}	1.382
	Zn^{2+}	4.44	4.71	22.32	6.82×10^{10}	0.896
	Fe^{3+}	2.29	3.56	28.07	5.28×10^{15}	1.725

[a] The rate constant was obtained at 20.51°C min^{-1} heating rate. The experiments were run at 800 psig, in N_2.

consistently lower. This could be explained by the shift in pH towards the higher values during the reaction, moving the upper part of the exotherms to higher temperatures, outside of the temperature range used in the experiments. This is important from the practical point of view, suggesting that the use of nitrates of too low acidity could result in only partial utilization of the oxidant in particleboard production.

Kinetic parameters

The kinetic parameters for the first exotherms are given in Table 4. Overall, the carbohydrates gave higher activation energies than lignins. The considerable variation in the kinetic parameters most likely results from the diverse natures of the lignocellulosics and nitrates used and the difficulty in maintaining the sufficiently uniform experimental conditions. A week negative correlation was obtained between the activation energies and reaction rate constants on one side and the pH values of the oxidation products on the other (Fig. 9). No explanation could be advanced for these relationships.

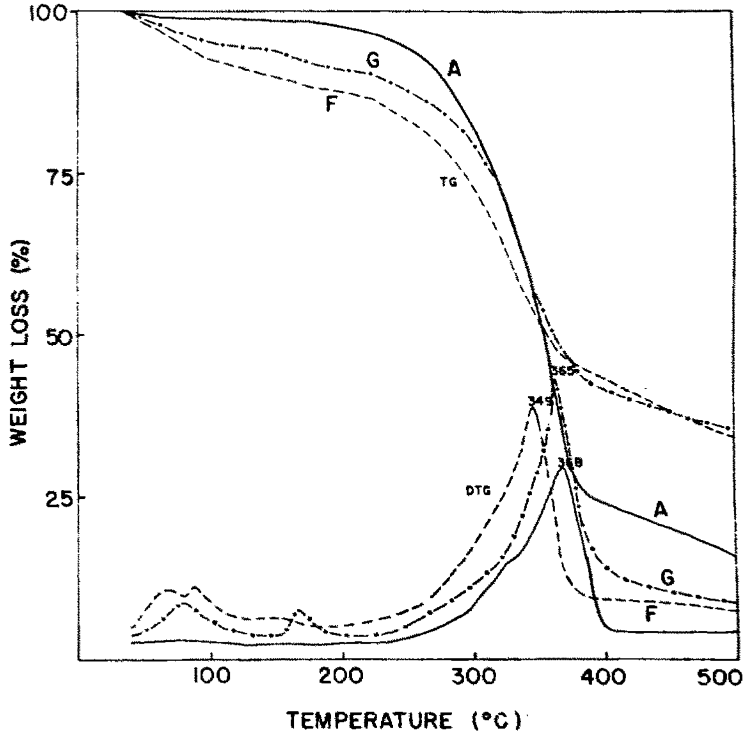


Fig. 10. TG and DTG curves for wood flour not treated (A), treated with $Fe(NO_3)_3$ (F), and treated with $Zn(NO_3)_2$ (G); 10°C min^{-1} in N_2.

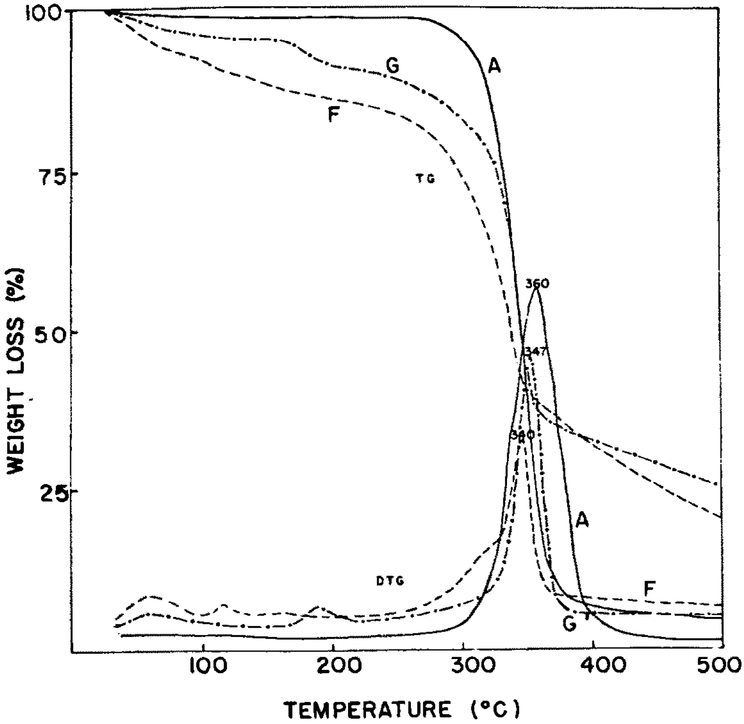


Fig. 11. TG and DTG curves for microcrystalline cellulose not treated (A), treated with $Fe(NO_3)_3$ (F), and treated with $Zn(NO_3)_2$ (G); 10°C min^{-1} in N_2.

TG and DTG analyses

The TG and DTG curves for wood flour, microcrystalline cellulose, and brown-rot lignin of softwood treated with ferric and zinc nitrates are given in Figs. 10–12. The DTG curves exhibit a pronounced peak corresponding to the first exotherm of the DSC curves. The peak is most likely caused by thermal decomposition of nitrates and oxidation of lignocellulosics, followed by evaporation of water and other volatile products formed during the reaction. The temperature of the maximum rate of weight loss is lower in the case of samples treated with nitrates and decreases as the acidity of nitrates increases. The relationships suggest that the oxidized lignocellulosics are less thermally stable than untreated lignocellulosics. Oxidative destabilization of polysaccharides has been noted by other workers using thermal analytical methods [18–20].

Infrared spectroscopy of oxidized lignocellulosics

Figures 13–15 give IR spectra of microcrystalline cellulose, precipitated cellulose, and brown-rot lignin of softwood oxidized with Al^{3+}, NH_4^+, Fe^{3+},

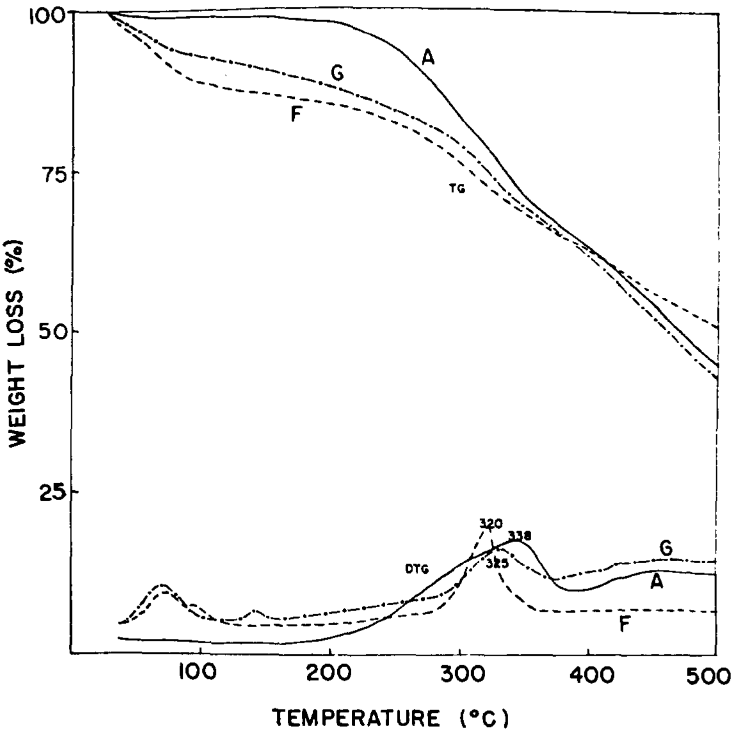


Fig. 12. TG and DTG curves for softwood brown-rot lignin not treated (A), treated with $Fe(NO_3)_3$ (F), and treated with $Zn(NO_3)_2$ (G); 10°C min^{-1} in N_2.

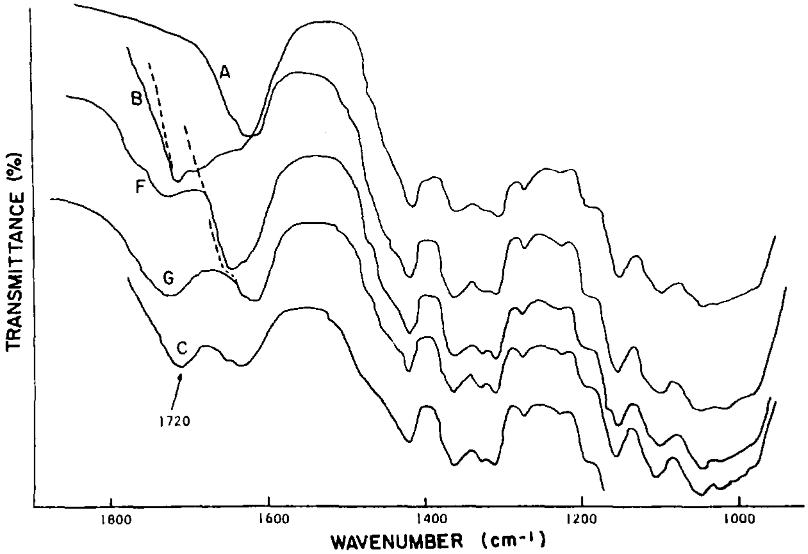


Fig. 13. Infrared spectra of microcrystalline cellulose not treated (A), treated with $Al(NO_3)_3$ (B), with $Fe(NO_3)_3$ (F), with $Zn(NO_3)_2$ (G), and with NH_4NO_3 (C) run on samples after completion of the first exothermic reaction. (———) After HCl treatment; (– – –) before HCl treatment.

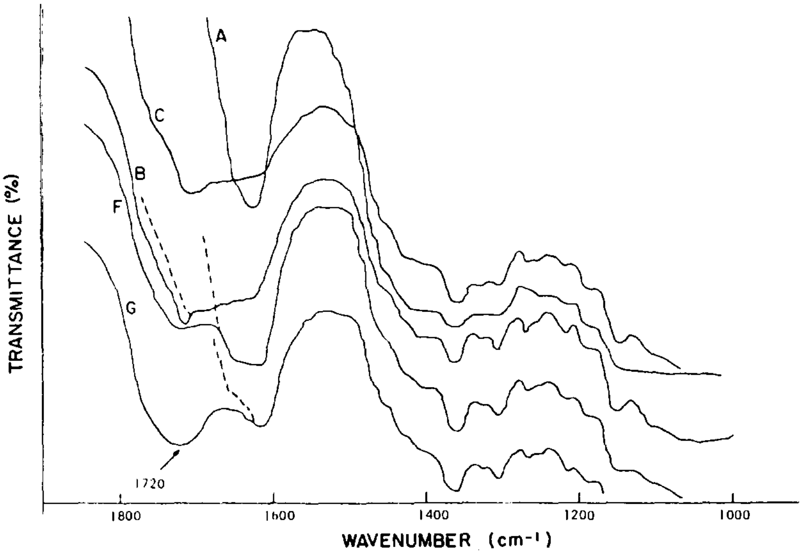


Fig. 14. Same as Fig. 13, only for precipitated cellulose.

and Zn^{2+} nitrates, respectively. The spectra differ from those obtained using nitric acid mainly by the absence of the ester bands at 1765 and 1740 cm^{-1} [2]. Treatment of the oxidized lignocellulosics with the vapor of concentrated HCl for 30 min and drying in vacuum for additional 30 min resulted in the appearance of carbonyl bands at around 1710–1725 cm^{-1} most likely due to COOH groups [21]. These changes can be best explained by the formation of

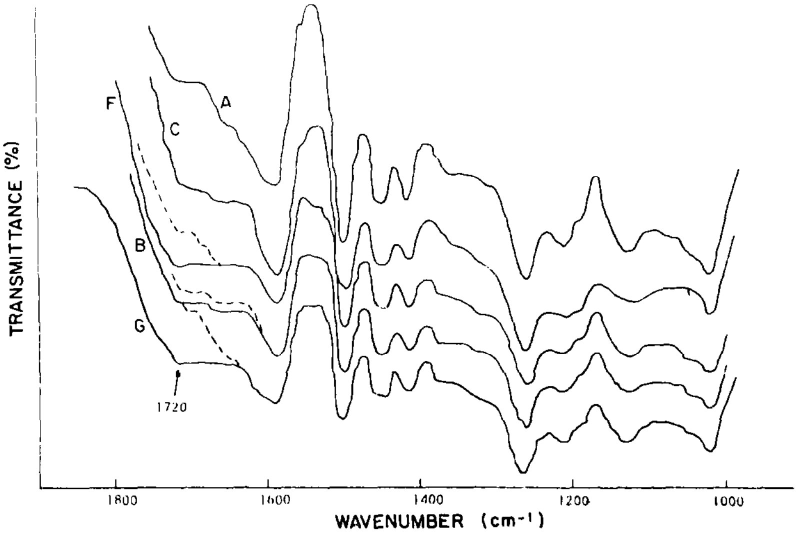


Fig. 15. Same as Fig. 13, only for softwood brown-rot lignin.

carboxylic acid salts as the result of oxidation with Al^{3+}, Fe^{3+}, and Zn^{2+} nitrates (bands at 1550–1610 and 1300–1420 cm^{-1}), with the acids liberated from the salts by the HCl treatment (bands at 1700–1725 cm^{-1}). It is interesting to note that the intensity of 1720 cm^{-1} band was stronger in precipitated cellulose than in microcrystalline cellulose, stressing the importance of accessibility of hydroxyl groups for the oxidation by nitrates.

The results suggest that use of nitrates rather than of nitric acid might influence the properties of the particleboard by an increased hygroscopicity imparted by the carboxylic salts formation as well as by the loss of a part of adhesion deriving from the ester bonds produced in nitric acid oxidations.

CONCLUSIONS

The results of DSC, TG, DTG, IR, and pH analyses of the interaction between nitrates and lignocellulosic materials indicated the existence of an oxidation reaction. A distinct linear relationship was obtained between the pH of the nitrate solutions and the temperature of the oxidation exotherm in DSC suggesting a close tie between the reactivity of the nitrate–lignocellulose mixtures and the pH values.

The IR analysis indicated the formation of the carboxylic salts as the oxidation products rather than of esters as was the case with nitric acid.

The TG and DTG data suggested that all oxidized lignocelluloses were less thermally stable than the nonoxidized original materials.

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