Thermogravimetric and Differential Thermal Analysis of Cellulose, Hemicellulose, and Lignin

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Synopsis

The thermal degradation of samples of cellulose, hemicellulose, and lignin have been investigated using the techniques of thermogravimetric analysis (TGA) and differential thermal analysis (DTA) between room temperature and 600°C. The results calculated from static and dynamic TGA indicated that the activation energy E for thermal degradation for different cellulosic, hemicellulose, and lignin samples is in the range 36-60, 15-26, and 13-19 kcal/mole, respectively. DTA of all the wood components studied showed an endothermic tendency around 100°C in an atmosphere of flowing nitrogen and stationary air. However, in the presence of flowing oxygen this endothermic effect was absent. In the active pyrolysis temperature range in flowing nitrogen and stationary air atmospheres, thermal degradation of Avicel cellulose occurred via a sharp endothermic and a sharp exothermic process, the endothermic nadir and exothermic peak being at 320° and 360°C, respectively. In the presence of oxygen, combustion of Avicel cellulose occurred via two sharp exothermic processes. DTA studies of different cellulose samples in the presence of air showed that the shape of the curve depends on the sources from which the samples were prepared as well as on the presence of noncellulosic impurities. Potassium xylan recorded a sharp exothermic peak at 290°C in a nitrogen atmosphere, and in a stationary air atmosphere it yielded an additional peak at 410°C, while in the presence of oxygen the curve showed two sharp exothermic peaks. DTA traces of periodate lignin in flowing nitrogen and air were the same and showed two exothermic peaks at 320° and 410°C, while in the presence of oxygen there were two exothermic peaks in the temperature range 200°-500°C.

INTRODUCTION

In a previous investigation,[1] the thermal degradation of cellulose, hemicellulose, and lignin was studied by dilatometric measurements. The temperature range covered was from the minimum temperature at which the samples gave off gas to about 15°-25°C above the minimum temperature. The dilatometric measurements could not be extended to higher temperatures because of experimental limitations. The decomposition temperature T_d was found to increase from 117° to 170°C in the order hemicellulose < lignin < cellulose.

The activation energy E, calculated for the initial stage of pyrolysis, varied from 46 kcal/mole for xylan to 150 kcal/mole for some samples of cellulose. The high activation energies obtained for cellulose were considered related to the highly ordered structure of cellulose.

In order to understand the effect of inorganic and organic chemicals on the thermal degradation of wood and its components at high temperatures, it is essential to know how the pure components themselves degrade. Therefore in this paper study of the thermal degradation of some of the samples used in the previous investigation,[1] together with other samples, has been carried out up to 600°C using the technique of thermogravimetric analysis (TGA) and differential thermal analysis (DTA). The results of the analyses are compared with those obtained by other investigators.

MATERIALS

The following samples were used:

Avicel P₂. A microcrystalline cellulose sample in the form of fine powder made from a special grade of wood pulp and supplied by American Viscose Corporation (now a division of Food Machinery and Chemical Corporation).

Cellulose R. A cellulose regenerated from a commercial diacetate sheet by treatment with 2% NaOH in a 50/50 mixture by volume of water and methanol.

Cellulose ICR-1. A bleached paper-grade softwood sulfite pulp supplied by International Cellulose Research.

Cellulose ICR-3. A bleached acetate-grade softwood sulfite pulp supplied by International Cellulose Research.

Birch Xylan. A sample prepared for a previous investigation[2,3] by direct extraction of birch wood meal with a solution of potassium hydroxide in an atmosphere of nitrogen. The xylan was used in the form of its potassium salt and the acid polysaccharide had a weight-average DP of 172 and a uronic acid content of 11.4%.

Douglas Fir Glucomannan. A sample prepared by extraction of holocellulose with NaOH containing 4% borate and precipitated by Ba(OH)₂; donated by Dr. G. G. S. Dutton, University of British Columbia.

Spruce Periodate Lignin. A sample prepared for previous investigation[4-6] by subjecting sawdust to cycles of periodate oxidation and hydrolysis.

Douglas Fir Klason Lignin. Prepared by digesting wood meal with 72% sulfuric acid and then subjecting it to hydrolysis.

EXPERIMENTAL

The TGA-DTA equipment was obtained from the American Instrument Company, Silver Spring, Maryland. In the case of dynamic and static TGA, experiments were carried out with a 200-mg sample under vacuum (30–50 μ). In dynamic TGA, the weight of the sample was recorded against temperature as the sample was heated at a rate of 4°C/min. For static TGA, four or five temperatures were chosen in the temperature range where there was a rapid loss of sample weight in the dynamic TGA. At

each of these temperatures the weight of a 200-mg sample was then recorded as a function of time.

DTA experiments were carried out with about 50 mg of sample in stationary air, flowing nitrogen and flowing oxygen atmospheres. The heating rate employed was 16°C/min while the flow rates of both oxygen and nitrogen were 20 ml/min. Experiments in the nitrogen and oxygen atmospheres were carried out after flushing the system with the respective gases at room temperature for 15 min. The sample and reference material holders were made of inconel alloy and were so designed that the inconel-sheathed, chromel–alumel thermocouples were in direct contact with the sample and reference material. Calcined alumina (Al_2O_3) was used as a reference material in all DTA experiments.

All the samples were dried under vacuum at 110°C and stored in a desiccator before carrying out the TGA and DTA experiments. For these experiments, periodate lignin, potassium xylan, glucomannan, cellulose R, ICR-1, and ICR-3 were cut in a Wiley mill to pass a $^1/_2$-mm sieve. Douglas fir lignin and Avicel-P_2 were in the form of fine powder which passed through 325- and 200-mesh sieves, respectively. All the dynamic TGA runs were done in duplicate, while most of the DTA runs were done in triplicate.

RESULTS AND DISCUSSION

Thermogravimetric Analysis

Figure 1 shows dynamic TGA curves of Avicel, periodate lignin, Klason lignin, potassium xylan, and glucomannan. The curves of ICR-1, ICR-3, and cellulose R resemble the Avicel curve and, to avoid crowding, are not shown in Figure 1.

Table I summarizes the temperature of onset and completion of active pyrolysis as well as the temperature of maximum pyrolysis. The temperatures of onset and completion of active pyrolysis are both defined as the

TABLE I
Dynamic Thermogravimetric Analysis of Various Wood Components

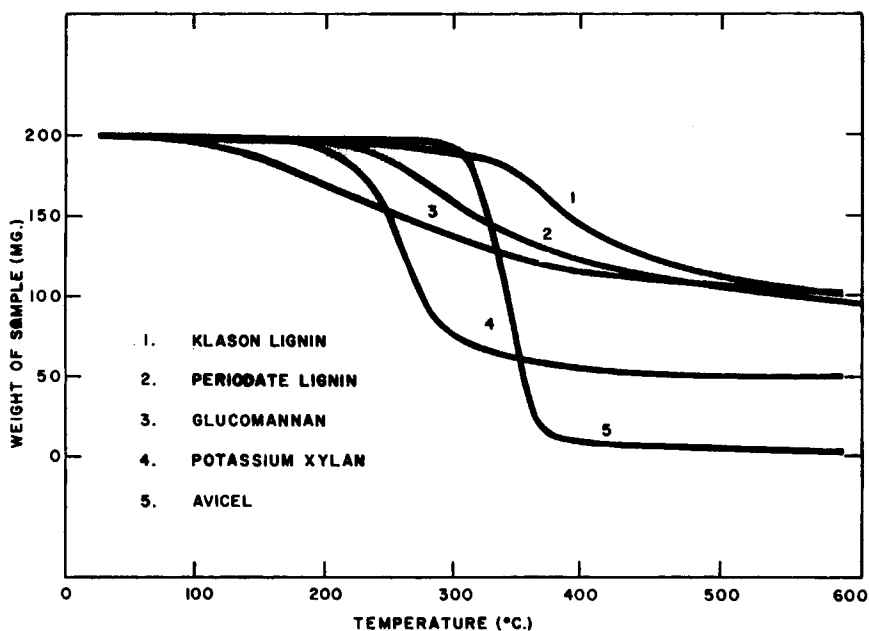| Sample	Temperature of active pyrolysis, °C			Volatilization, %			
	Initial	Maximum	Final	250°C	300°C	350°C	400°C
Avicel cellulose	295	345	380	1	4	64	95
ICR-1	280	250	380	3	7	52	86
ICR-3	300	350	385	2	5	55	90
Cellulose R	245	280	320	7	39	47	54
Potassium xylan	195	260	325	32	62	69	72
Glucomannan	140	—	310	25	32	38	43
Periodate lignin	230	295	390	9	21	32	40
Klason lignin	320	375	440	3	5	12	30

Fig. 1. TGA curves of Avicel cellulose, periodate lignin, Klason lignin, potassium xylan, and glucomannan under vacuum. Sample weight 200 mg, heating rate 4°C/min, vacuum 30–50 μ: (1) Klason lignin; (2) periodate lignin; (3) glucomannan; (4) potassium xylan; (5) Avicel.

temperature at which the rate of weight loss of a 200-mg powdered sample heated at 4°C/min is 1 mg/min. Comparing the temperatures of onset of active pyrolysis, hemicelluloses were found to be the least thermally stable. This is in agreement with the results obtained by Ramiah and Goring,[1] Tang,[7] and Kosik et al.[8]

Klason lignin is found to be more thermally stable then periodate lignin, the onset of active pyrolysis of Klason lignin starting at a higher temperature than that of Avicel. The difference in the stability of the two lignins could be due to the difference in their preparation as well as in the detailed chemical structures. In the periodate lignin prepared by mild alkali treatment of oxidized wood, it is reported that the pendant guaiacyl residue with free phenolic groups is destroyed, causing opening of the benzene ring.[9] Also it is known that in the preparation of Klason lignin extensive condensation takes place during the acid treatment. Therefore the thermal stability of lignins depend on the method of their isolation, although weights of residual char for the two lignins at the end of pyrolysis remain the same.

In the case of the two hemicelluloses, xylan was found to be much more stable than glucomannan. This could be due to the difference in their structures and molecular weights. Xylan is essentially a linear chain, built up of xylose units with d-glucuronic acid attached to every tenth
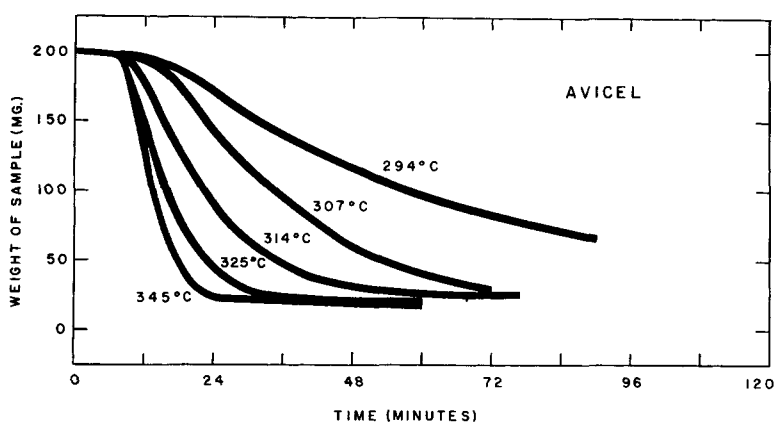
Fig. 2. Static TGA curves for Avicel cellulose at different temperatures under vacuum. Sample weight 200 mg, vacuum 30–50 μ.

xylose unit, on an average as a side group in the chain, while glucomannan is a linear chain of glucose and mannose.

Cellulose R shows the least thermal stability of the cellulose samples studied. Reasons for this could be the decrease in crystallinity of the regenerated cellulose and also some degradation taking place during the acetylating and deacetylating processes.

Figure 2 shows static TGA runs for Avicel at five different temperatures, similar curves being obtained for potassium xylan and periodate lignin.

Calculation of Activation Energy E

Assuming first-order reaction for thermal degradation, the reaction rate constant k and the activation energy E for the degradation were calculated by static and dynamic TGA.

In static TGA, the reaction rate constant k at a particular temperature was obtained as a least-square plot of log of residual weight versus time. In mathematical form, the relation can be written as

$$k = \frac{\ln (1 - W_t/W_d)}{t} \tag{1}$$

where W_t = weight loss at the end of t minutes; and W_d = weight loss at the end of pyrolysis, which was taken as the weight loss at the end of 4 hr when a 200-mg sample was heated at the temperature of maximum rate of pyrolysis.

The activation energy E for thermal degradation is obtained from the following relation between E and the rate constant k:

$$k = Ae^{-E/RT} \tag{2}$$

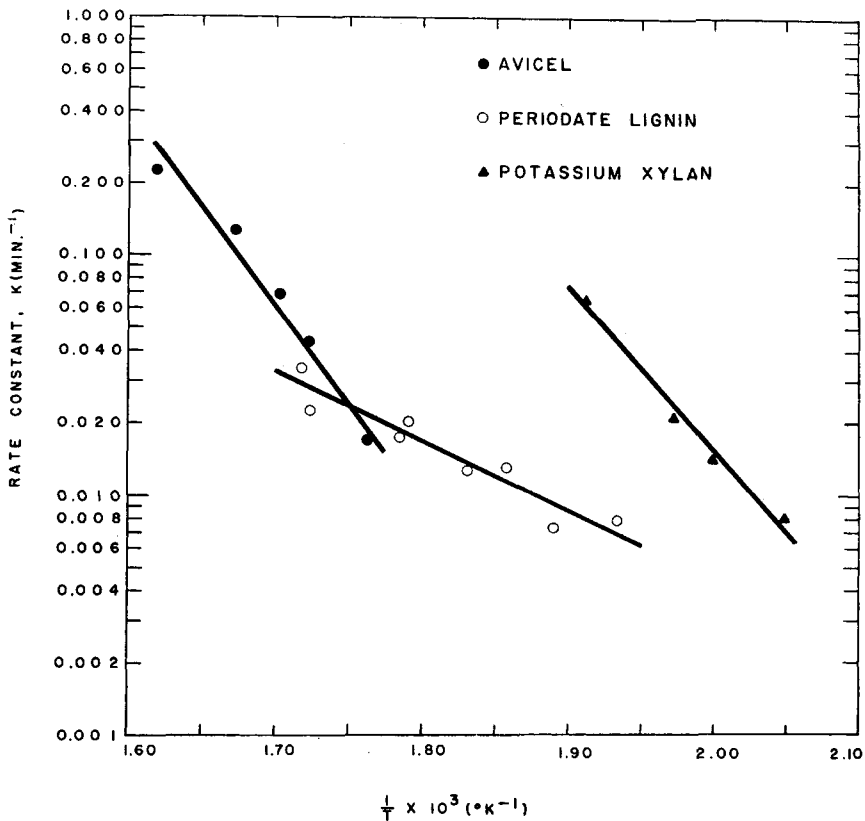where A = frequency factor, R = gas constant, and T = absolute temperature.

Fig. 3. Arrhenius plot for Avicel cellulose, periodate lignin, and potassium xylan from data of static TGA: (●) Avicel; (O) periodate lignin; (▲) potassium xylan.

Thus, from the least-square slope of the plot of log k versus the reciprocal of absolute temperature, E was calculated for Avicel, xylen, and periodate lignin as shown in Figure 3.

The data obtained by dynamic TGA were analyzed by the differential method used by Tang.[7] In the differential method, the rate of weight loss and reaction rate constant k at various temperatures were calculated from the relations

$$\frac{dw}{dt} = \left(\frac{dw}{d\tau}\right)\left(\frac{d\tau}{dt}\right) \tag{3}$$

$$\frac{dw}{dt} = kw_r \tag{4}$$

where dw/dt = weight loss per minute, $dw/d\tau$ = weight loss per °C, and $d\tau/dt$ = rate of temperature rise per minute. The residual weight of sample at temperature τ, w_r, is obtained from the relation

$$w_r = w_d - \bar{w} \tag{5}$$

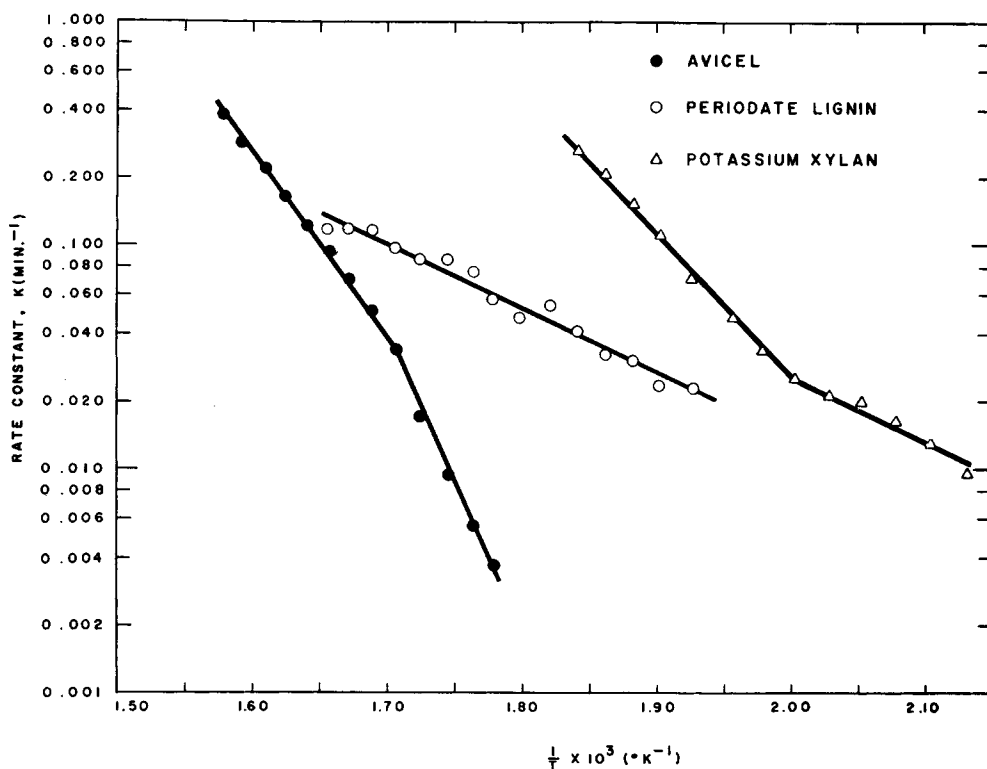where $\bar{w}$ is the weight loss at temperature τ.

Fig. 4. Arrhenius plot for Avicel cellulose, periodate lignin and potassium xylan from data of dynamic TGA: (●) Avicel; (○) periodate lignin; (△) potassium xylan.

The E value can thus be calculated from the least-square slope of the plot of log k versus reciprocal of absolute temperature, as shown in Figure 4. As can be seen from this figure, a dual segment approximation was necessary in the case of Avicel and potassium xylan. This indicates that pyrolysis takes place by two mechanisms in the temperature range studied, while degradation of periodate lignin could be explained by a single mechanism.

The static and dynamic TGA methods were used for calculating E in the case of Avicel, periodate lignin, and potassium xylan. For the rest of the samples, E was calculated only by dynamic TGA. The main disadvantage in the static method for calculating E is that there is an excessive loss of weight before the sample reaches the pyrolysis temperature; i.e., the higher the temperature, the greater is the weight loss. In the present investigation it was found that the time taken by the sample to reach the pyrolytic temperature was 12 to 15 min.

The pyrolytic reaction of cellulose up to about 40% initial decomposition was reported to be very complex and could not be explained by a simple reaction law.[10,11] Tang and Neil,[12] using dynamic TGA, observed a zero-

to first-order initial reaction. E for Avicel cellulose calculated by the static method (35 kcal/mole) agrees well with 37 kcal/mole obtained for cotton cellulose[10] and 34–42 kcal/mole for α-cellulose.[13-15] Further, the higher value of E (60 kcal/mole) calculated by the dynamic differential method for the lower temperature range could be due to the complexity of the reaction during initial weight loss. Chatterjee and Conrad[10] have proposed a new reaction mechanism for cellulose decomposition. They considered the major reaction as a two-step process, with an initiation step as glucosidic-bond scission and levoglucosan formation as the propagation step. Further, they claim all the E values reported for cellulose, by static TGA based on first-order plot, are only for the propagation step of cellulose decomposition.[10,13-15]

The other cellulosic samples gave a single line in the Arrhenius plot over the calculated temperature range. This could be due to one or more reasons: (1) ICR-1 and ICR-3 had some hemicelluloses present in them as impurities[1]; (2) cellulose R, as mentioned earlier, must have lost its crystallinity during acetylation and subsequent deacetylation.

In the case of xylan, the dual-segment Arrhenius plot was different from that of Avicel, showing a greater E (26 kcal/mole) value at the higher temperature range. Further, the E value calculated by the static method (30 kcal/mole) agreed with the value in the higher temperature range. Also Kosik et al.[8] found that the degradation of beechwood 4-O-methyl-glucurono-xylan takes place via two mechanisms in the temperature range 100° to 290°C, the values in the first and second stages being 11 and 21 kcal/mole, respectively. E value calculated for Douglas fir glucomannan was exceptionally low and has, therefore, not been reported in this paper. This low value could be either due to the difference in the mechanism of

TABLE II
Energy of Activation E for Thermal Degradation of Different Wood Components

	Static thermogravimetry		Dynamic thermogravimetry	
Sample	E, kcal/mole	Temperature, °C	E, kcal/mole	Temperature, °C
Avicel	35 ± 4	294–345	60 ± 2[a]	285–320
cellulose			39 ± 1[a]	320–360
ICR-1			46 ± 1[a]	300–361
ICR-3			47 ± 1[a]	282–361
Cellulose R			36 ± 2[a]	258–282
Potassium	30 ± 2	215–250	15 ± 2[b]	195–225
xylan			26 ± 1[b]	225–265
Periodate	13 ± 2	244–309	13 ± 1[a]	245–330
lignin				
Klason			19 ± 1[a]	319–385
lignin				

[a] Average values of two determinations. The error reported is the mean of standard deviation.

[b] Average values of four determinations.

thermal degradation compared to the rest of the components studied, or it may be due to some unidentified impurities present in the sample. More TGA data with different glucomannan samples are needed to obtain the true E value. E values calculated for periodate lignin by static and dynamic methods were the same (13 kcal/mole). Klason lignin gave an E value of 19 kcal/mole, close to that of periodate lignin. The exact mechanism of xylan and lignin degradation is not known and would be expected to be quite complicated. Table II summarizes the E values of different wood components.

Differential Thermal Analysis

Figures 5 to 7 show the comparison of DTA curves in flowing nitrogen, static air, and flowing oxygen atmospheres of samples of Avicel cellulose, periodate lignin, and potassium xylan. Figure 8 demonstrates the DTA curves of different cellulosic samples in static air.

In the presence of nitrogen (Fig. 5), Avicel cellulose showed a similar DTA curve to that observed by Broido[16] for ash-free cellulose. The endothermic nadir around 100°C is due to the evaporation of monomolecularly adsorbed water which could not be removed completely on drying. The endothermic shoulder appearing around 170°C must be mainly due to a dehydration process involving the splitting off of a hydroxyl group and of a hydrogen between two hydroxyl groups to form water. Broido observed this shoulder at 220°C. He used ash-free filter paper as his cellulosic sample instead of the microcrystalline cellulose used in this investigation. Therefore the difference could be due to the different type of sample used.

It already has been shown that pyrolysis of Avicel cellulose occurs via two different mechanisms in the temperature range 280° to 360°C, as indicated in Figure 4. The DTA curve (Fig. 5) also shows that thermal degradation occurs via an endothermic process between 280° and 300°C and an exothermic process between 320° and 360°C, similar to the observation of Broido.[16] In the case of DTA in static air (i.e., in the presence of a limited amount of oxygen), Avicel behaved like in a nitrogen atmosphere except that the slight endothermic effect around 170°C was reduced. From Figure 8 it is evident that, although the curve of cellulose R has the same shape as that of Avicel cellulose, the endothermic to exothermic transition takes place at a lower temperature. This is because the active pyrolysis takes place at a lower temperature, as shown in Table I. DTA curves of ICR-1 and ICR-3 were different from Avicel and cellulose R, and the reason is possibly due to the fact that each of the two samples was made from a different grade of pulp having different amounts of hemicellulose present as impurities. Broido also showed that the DTA curves of cellulose are very sensitive to impurities. He found that a cellulose sample with 0.01% ash content gave a sharp endotherm and an exotherm at about 320° and 360°C, respectively, while a sample with 0.15% ash showed a broader endotherm at 320°C and only a shoulder at 360°C. Further, cellulose containing 1.5% $KHCO_3$ showed no endotherm at all.
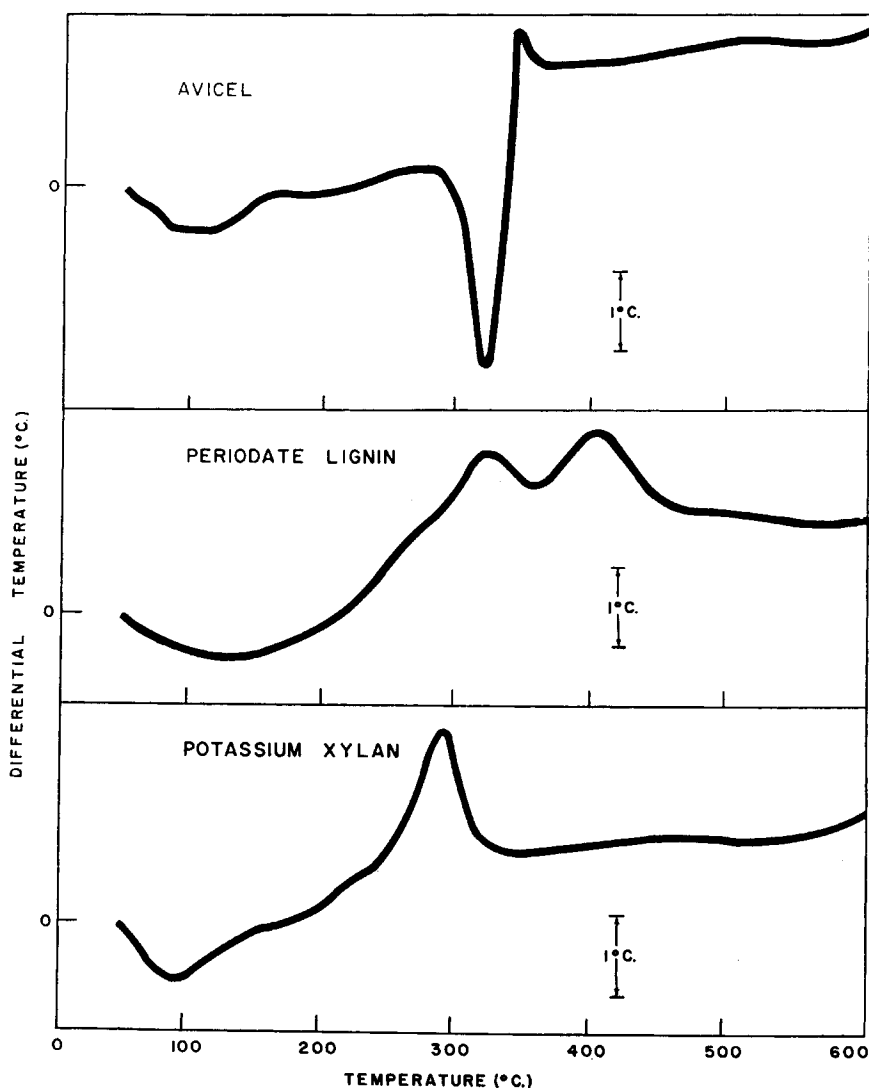
Fig. 5. DTA curves of Avicel cellulose, periodate lignin, and potassium xylan in nitrogen. Sample weight approximately 50 mg, heating rate 16°C/min, nitrogen flow rate 20 cc/min.

In the presence of oxygen, Avicel showed no endotherm at 100°C, but yielded an exothermic peak at about 360°C as observed in nitrogen and air atmospheres, together with a new peak at about 480°C which must be due to the oxidation of the degraded fragments of cellulose at more than 360°C.

Potassium xylan in nitrogen atmosphere produced an endothermic nadir at about 100°C and two exothermic reactions starting at 225°C and peaking at 290°C. The 100°C endothermic nadir must be due to the evaporation of water. It is hard to visualize a dehydration process for
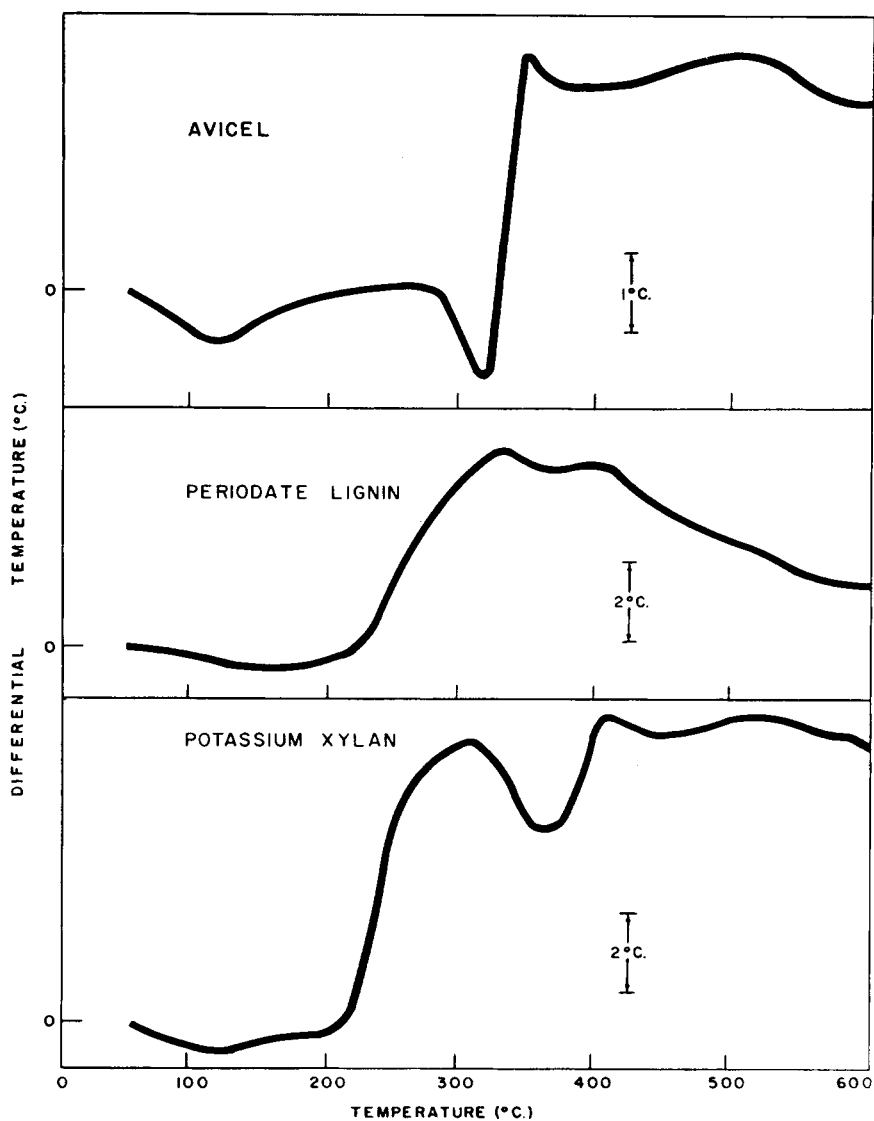
Fig. 6. DTA curves of Avicel cellulose, periodate lignin, and potassium xylan in static air. Sample weight approximately 50 mg, heating rate 16°C/min.

xylan similar to that for cellulose to explain the slight endothermic shoulder at 170°C. Xylan does not have any primary OH groups as does cellulose. It is unlikely that a dehydration involving secondary OH groups can take place. This temperature, however, could correspond to the softening of xylan, and it is also interesting to note that Goring[17] found that dry potassium xylan softened at 167°C. The shoulder in the range 200° to 225°C was due to slower pyrolysis, as shown in the Arrhenius plot of Figure 4, and the beginning of the exothermic reaction at 225°C corresponding to the
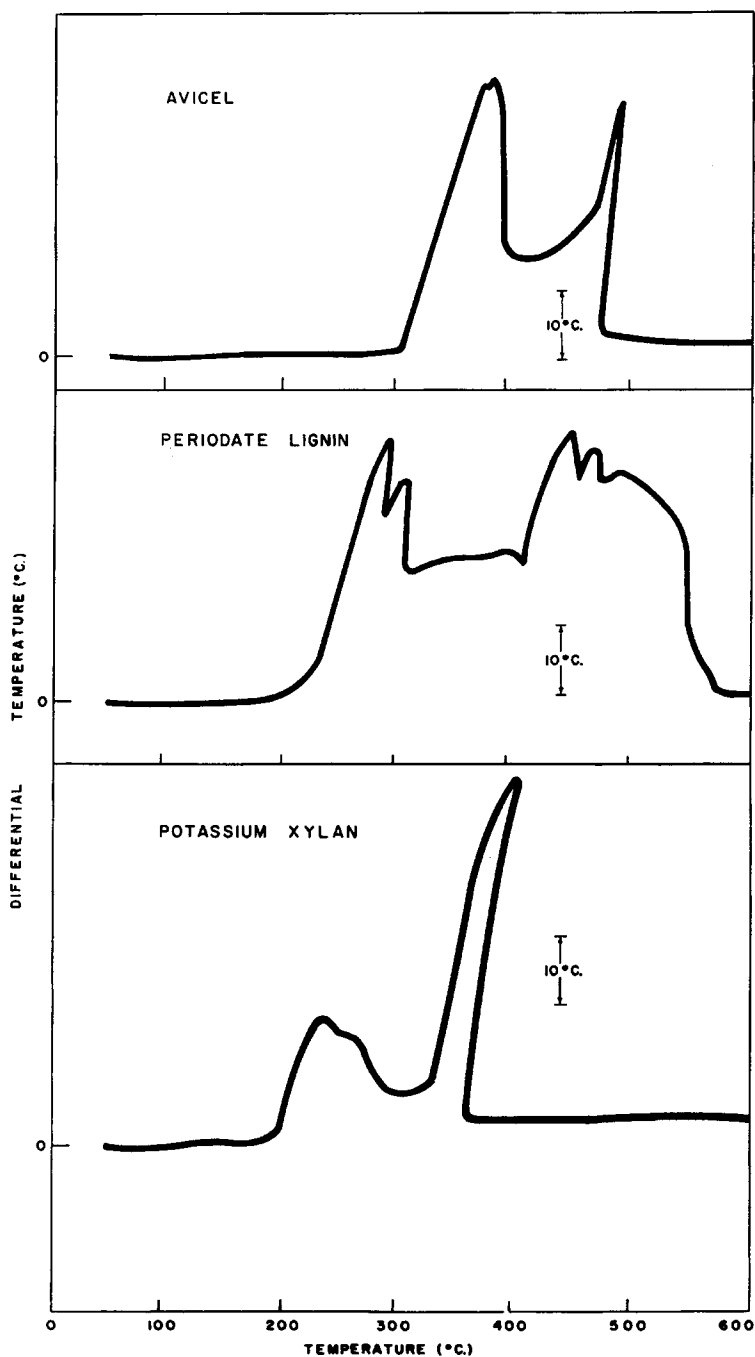
Fig. 7. DTA curves of Avicel cellulose, periodate lignin, and potassium xylan in oxygen. Sample weight approximately 50 mg, heating rate 16°C/min, oxygen flow rate 20 cc/min.
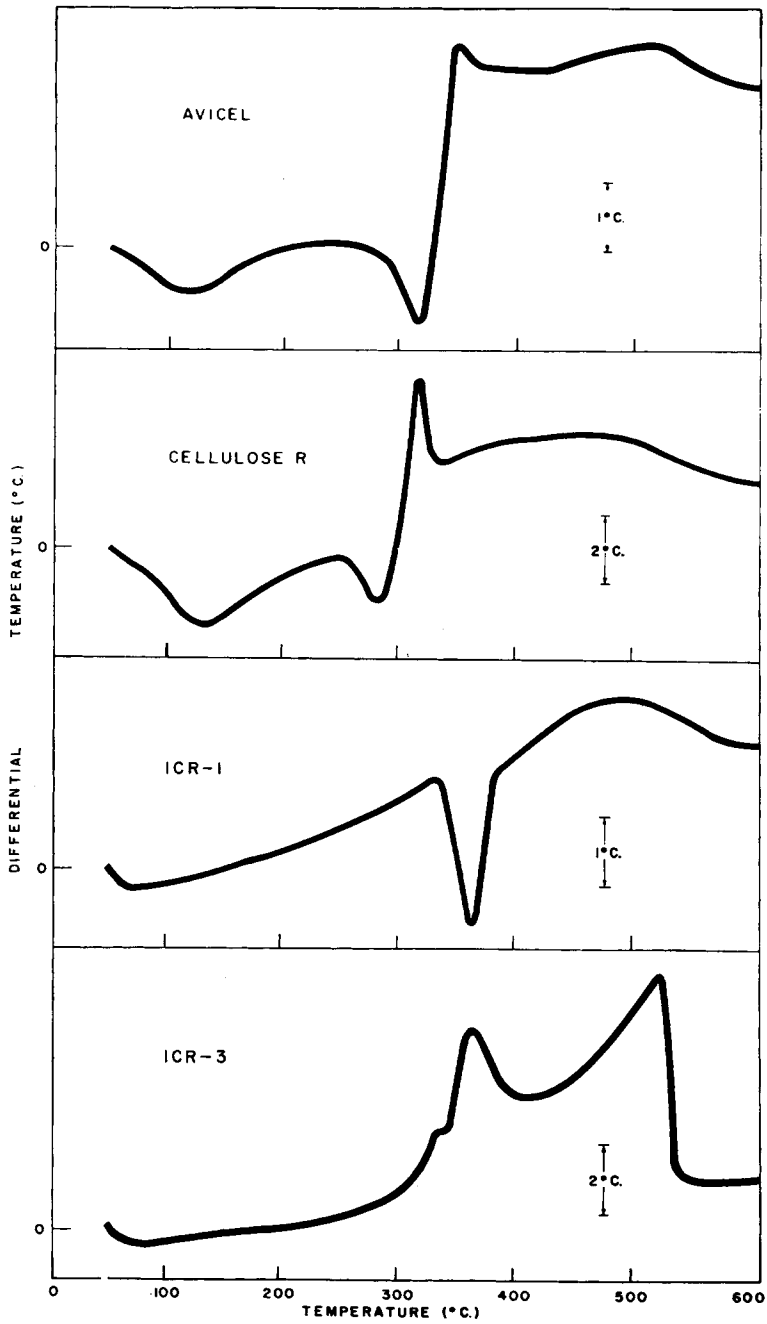
Fig. 8. Comparison of DTA curves of Avicel cellulose, cellulose R, ICR-1, and ICR-3 in static air. Sample weight approximately 50 mg, heating rate 16°C/min.

beginning of fast pyrolysis. In static air atmosphere, xylan showed an exothermic peak around 410°C, in addition to the one at 300°C observed in nitrogen atmosphere. The second peak could be due to the restricted oxidation of degraded products of xylan. In oxygen, the lower exothermic reaction started at about the same temperature as in air, but the peak occurred at a lower temperature. The second peak occurred at the same temperature as in air, but it was much sharper indicating complete oxidation of the decomposed xylan.

DTA study of periodate lignin showed that in the presence of nitrogen the degradation occurred via two exothermic processes in the range 235° to 400°C which corresponded to the active pyrolysis range in TGA studies (Table I). In the static air atmosphere, the shape of the curve remained the same but the two exothermic effects were greatly increased. In flowing oxygen, periodate lignin indicated two twin exothermic peaks, one near 280°C and the other near 450°C. As in the case of xylan, the presence of oxygen lowered the temperature of the initial exothermic peak, but the second exothermic reaction took place at a higher temperature. This perhaps could be due to the difference in the nature of the products formed at the end of initial exothermic reaction.

CONCLUSION

Thermogravimetric analyses of cellulose, hemicellulose, and lignin under vacuum have shown that Douglas fir Klason lignin is the most thermally resistant. Cellulose is intermediate and the hemicelluloses are the least stable. The lower thermal stability of periodate lignin is attributed to considerable chemical degradation of the native lignin during periodate oxidation. The activation energy E for thermal degradation of the samples were in the order cellulose > hemicellulose $\geq$ lignin.

The DTA studies in nitrogen flow and stationary air atmospheres indicated that the thermal degradation of Avicel cellulose takes place via an endothermic process, followed by an exothermic process; while in the presence of oxygen, combustion occurs via two exothermic processes. It has been confirmed that the presence of different amounts of impurities affect the thermal analysis curve of cellulose samples appreciably. In the case of potassium xylan in stationary air atmosphere, the appearance of a second exothermic peak around 410°C was attributed to the controlled oxidation of the decomposed products of xylan at about 290°C. In the presence of oxygen, xylan also showed that combustion occurred via two distinct exothermic processes. DTA of periodate lignin in flowing nitrogen and static air showed that decomposition took place via two exothermic processes; while in the presence of oxygen, the curve showed four exothermic peaks, indicating that combustion reaction of the lignin is quite complicated.

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