

MECHANISM OF THERMAL DECOMPOSITION OF LIGNIN

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ABSTRACT

Differential thermal analysis studies of milled wood lignin and lignin carbohydrate complex at different heating rates showed three exothermic peaks. The heating rate is the factor that affects their sharpness and position. The peaks are sharp at low heating rates. Infrared spectra and scanning electron micrographs of the pyrolyzed lignin residues show that aliphatic scission of the lignin molecule at the onset of pyrolysis and progressive carbonization of the surface are the principal features of degradation; there is no intermediate compound formed during the pyrolysis.

Keywords: Milled wood lignin, lignin carbohydrate complex, decomposition, thermal analysis, degradation, infrared spectroscopy, scanning electron micrographs.

INTRODUCTION

Combustion of wood, cellulose, and lignin is preceded by pyrolysis where gaseous and liquid products are formed as well as a solid residue of charcoal. Some of the gases and liquids, when mixed with air, burn with a flame, whereas the charcoal burns in air by glowing without flame. Much has been published on the destructive distillation and carbonization of wood, with particular reference to the products formed under specific conditions; extensive studies have also been made of the pyrolytic depolymerization and decomposition of cellulose.

Little information is available on the thermal analysis of lignin. Some studies of the pyrolysis of lignin have been made in relation to the flammability of wood (Domansky and Rendos 1962; Sandermann and Augustin 1964; Tang and Neill 1964). One reason for this is that lignin itself is not yet of much commercial interest. Although it is likely that changes are induced during preparation of lignin from wood, thermal degradations of different lignin preparations all show essentially the same features (Domansky and Rendos 1962).

Lignin strongly influences the pyrolysis and combustion of wood. In thermal analysis, wood behaves approximately as if it was a mixture of cellulose, hemicellulose, and lignin (Eickner 1962; Stamm 1962). Differential thermal analysis (DTA) characterization of lignin shows that lignin pyrolyzes more slowly than wood (Tang 1967; Tang and Eickner 1968). In the absence of oxygen, the thermal stability is in the order: lignin, cellulose, hemicellulose (Sandermann and Augustin 1963). In the combustion of wood, the cellulose fraction contributes most to the flaming combustion, whereas the lignin fraction supports the subsequent glowing combustion (Brown 1958; Tang and Eickner 1968).

A detailed study on the mechanism of lignin pyrolysis is thus needed to complete the picture of the flammability and pyrolysis of wood. This present work was undertaken for this purpose.

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TABLE 1. DTA curves of different lignin preparations at different heating rates (inert atmosphere).

Endothermic	Exothermic	Heating rate, C/min	Reference
100–180	280–300 ¹ & 400 ²	—	8
125	345–500	12	22
—	290–380 ¹ & 420 ²	6	2
100–200	390–400	6	18
	MWL		
50–210	220–300 ¹ & 350 ²	0.5	The present work
50–220	240–330 ¹ , 360–370 ² & 430 ³	2	The present work
50–210	220–540	10	The present work
	LCC		
50–220	240–300 ¹ , 350 ² & 410 ³	0.5	The present work
50–260	260–340 ¹ , 380 ² & 450 ³	2	The present work
50–240	240–380 ¹ , 380–410 ² & 480 ³	10	The present work

¹ First peak in the DTA curve.² Second peak in the DTA curve.³ Third peak in the DTA curve.

EXPERIMENTAL

The lignin samples used were milled wood lignin (MWL) and lignin carbohydrate complex (LCC) from black spruce (Brownell 1968, 1970).

The DTA thermograms were obtained using a Tracer Inc. (Al-stone Company) Model 202 differential thermal analyzer with temperature programmed at 0.5, 2 and 10 C/min heating rate, from room temperature to 600 C. Helium gas was used as an inert medium during the thermal analysis; the flow rate was 0.025 ft³/h at atmospheric pressure. The amount of material used was 23 mg. The reference material was aluminum oxide.

Lignin residues were obtained by stopping the pyrolyzing reaction in the DTA equipment at 190, 280, 380 and 460 C.

The infrared spectra for the different pyrolyzed lignin residues were obtained on potassium bromide disks (0.5–1% sample) with a UNICAM SP1000 Infrared Spectrophotometer.

A scanning electron microscope (model AMR-1000) was used to obtain micrographs of the pyrolyzed lignin residues. The best magnification was found at 500 and 1,500 times.

RESULTS AND DISCUSSION

Domansky and Rendos (1962) compared the DTA curves of different lignin preparations in vacuo and concluded that the degradation pattern was virtually the same for each. An endotherm extended from about 100 to 180 C and was followed by an exotherm at about 400 C. The results of thermal analysis of individual types of lignin made by many other investigators (Berkowitz 1957; Domansky and Rendos 1962; Tang and Eickner 1968), Table 1, show peaks falling within the same ranges. However, these studies did not examine the effect of heating rate.

On changing the heating rate from 0.5 to 10 C/min, sharp peaks appeared in the thermogram of MWL (Figs. 1–3). Detailed studies of the DTA curves (Fig.

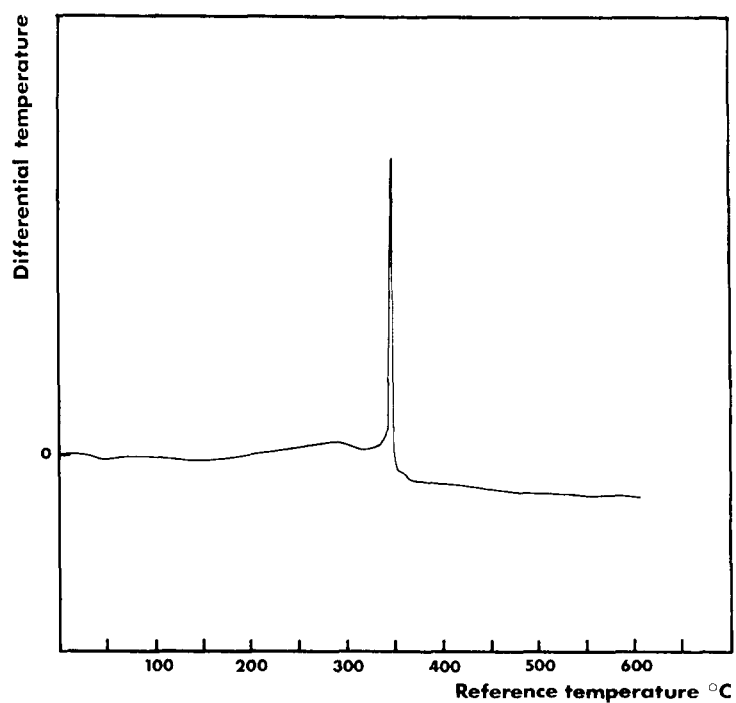


FIG. 1. DTA curve for MWL at 0.5 C/min.

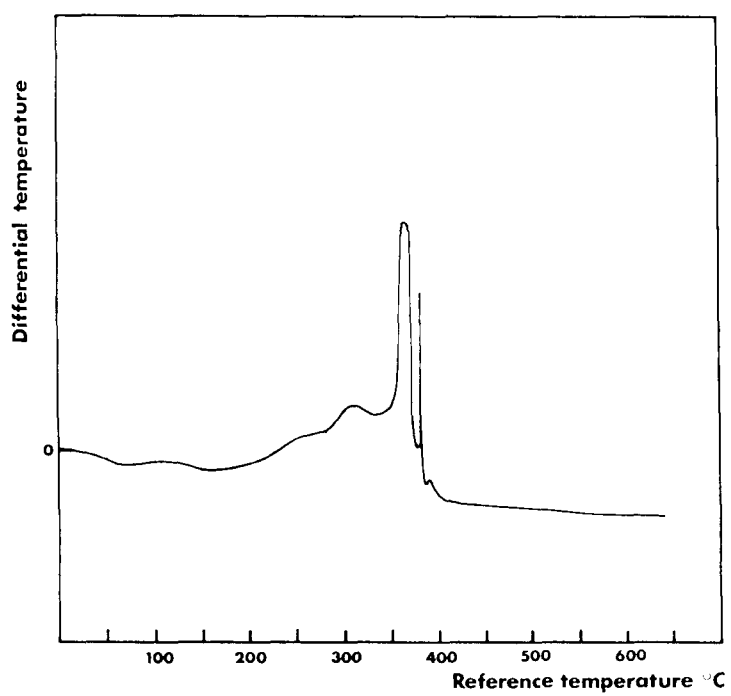


FIG. 2. DTA curve for MWL at 2 C/min.

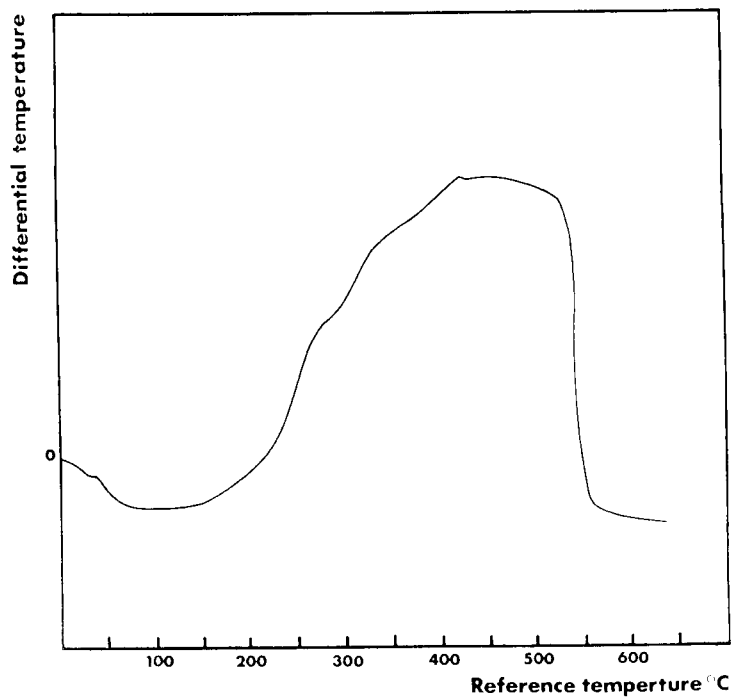


FIG. 3. DTA curve for MWL at 10 C/min.

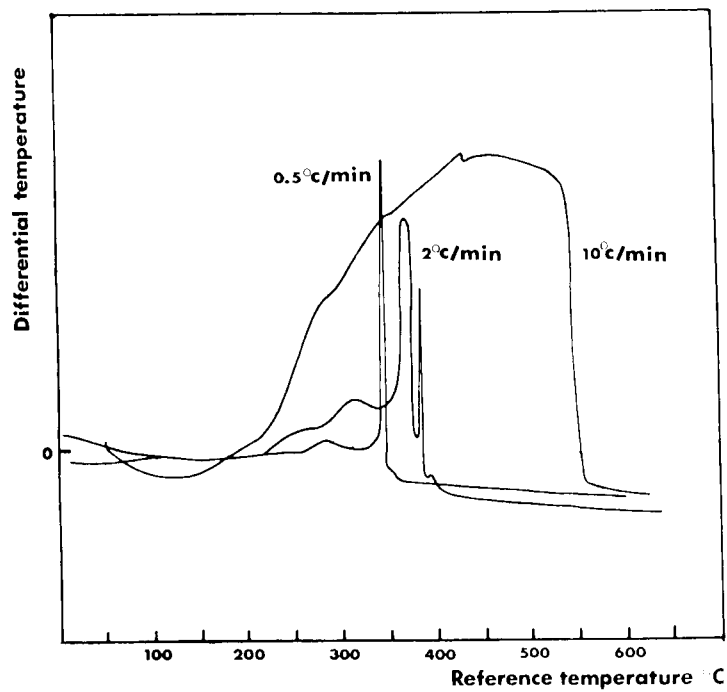


FIG. 4. DTA curve for MWL at different heating rates.

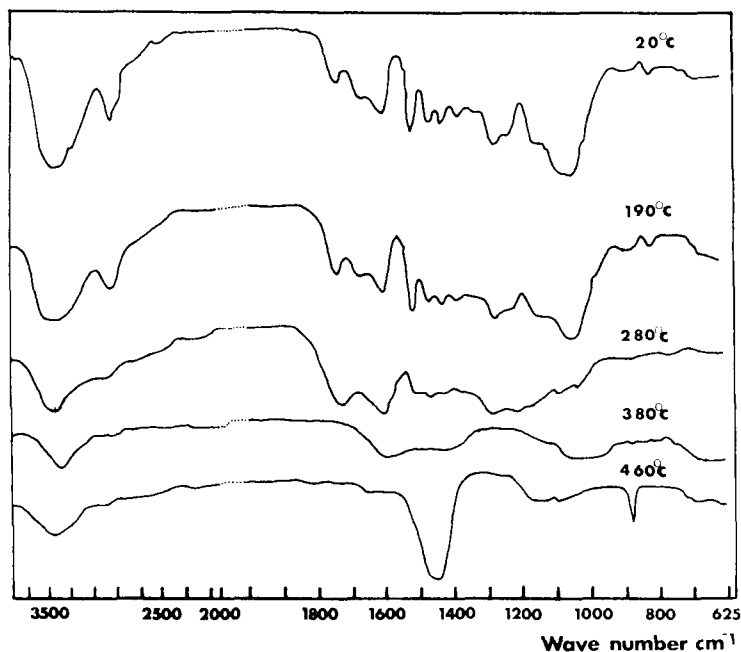


FIG. 5. Infrared analysis of MWL and its pyrolyzed residues.

4) show that the endothermic reactions start at about 50 C and end at about 200 C, with a nadir shifting to lower temperature as the heating rate is increased (170 C for 0.5 C/min, 150 C for 2 C/min, and 130 C for 10 C/min). The exothermic reactions appear as three peaks. The first exothermic peak is low and broad and shifts to a higher temperature as the heating rate is increased. The peaks are situated between 220 and 300 C for 0.5 C/min and between 240 and 330 C for 2 C/min (the peak for both heating rates is at about 280 C), while at 10 C/min heating rate the exothermic peak starts at 220 C and ends at 540 C. The first exothermic peak is in agreement with the findings of other investigators (Table 1). The second exothermic peak is sharp and shifts to higher temperature at increased heating rate.

At a heating rate of 0.5 C/min, the second peak is very sharp at 350 C. At 2 C/min, the second peak is well defined in a very narrow temperature range, 360 and 370 C, and another peak is very sharp at 380 C; a third peak can also be seen at 450 C. At the faster heating rate (10 C/min), there is only one broad exothermic peak obscuring all the forementioned peaks. It starts at 220 C and ends at 540 C, nearly in the same range found by Berkowitz (1957) for Klason lignin at 6 C/min.

Infrared (IR) spectra and scanning electron micrographs of the lignin residues pyrolyzed at different temperatures were obtained.

It seems that the endothermic nadir is due not only to driving off moisture and absorbed gases but may also be related to the softening and melting of the lignin. The lignin softening point is about 170 C (Bjorkman and Person 1956). The endothermic nadir is due to the dual effect of driving off the absorbed gases and

TABLE 2. *Infrared absorption bands for the pyrolyzed MWL residues.*

Wave number, cm ⁻¹	Functional groups	Remarks on the absorption bands
3,400	Bonded OH (Hergert 1960; Pearl and Busche 1960)	Appeared in all (280, 380, & 460 C) but decreased in intensity on heating.
2,980	Aliphatic C-H bonds (Hergert 1960; Pearl and Busche 1960)	Very small at 280 and 380 C and disappeared at 460 C.
1,730	Carbonyl group (Pearl and Busche 1960; Pilichuk et al. 1966)	Small at 280 C and disappeared at 380 and 460 C.
1,670	Ald. or keto carbonyl (Hergert 1960; Pearl and Busche 1960)	Disappeared at 280, 380, and 460 C.
1,600	Aromatic nucleus (Hergert 1960; Pearl and Busche 1960; Sarkanen and Chang 1967)	Present at 280, very small at 380 and disappeared at 460 C.
1,520	Unconjugated guaiacyl nucleus (Hergert 1960; Sarkanen and Chang 1967)	Very small at 280, disappeared at 380 and 460 C.
1,470	Guaiacyl and syringyl units (Bolker and Soverville 1963)	Very small at 280 and disappeared at 380 and 460 C.
1,380	CH ₃ -O (Hergert 1960)	Disappeared at 280, 380, and 460 C.
1,275	Uncondensed guaiacyl nuclei and methoxyl group (Hergert 1960; Sarkanen and Chang 1967)	Very small at 280 and disappeared at 370 and 460 C.
1,230	Phenolic hydroxyl and C-O alkyl-aryl ether (Hergert 1960)	Present at 280 and disappeared at 380 and 460 C.
1,110-1,020	Primary and secondary alcohol groups (Hergert 1960)	Disappeared at 280, 380, and 460 C.
820	Two adjacent aromatic C-H bonds (Hergert 1960; Liang et al. 1960)	Very small at 280 C and disappeared at 380 and 460 C.

the softening effect of lignin. Generally, at the end of the endothermic period at about 190 C, the lignin powder becomes one mass. There is no major change in the IR spectrum of lignin on heating to 190 C (Fig. 5), but scanning micrograph shows the lignin particles sticking together (Fig. 7).

The results in Table 1 and Figs. 1-4 show that generally there are three exothermic DTA peaks. The IR spectrum of MWL (Fig. 5) for the pyrolyzed lignin residue of the first peak (at 280 C) shows a disappearance of the absorption bands at wave numbers 1,670, 1,380, and 1,100-1,020 cm⁻¹ and a diminishing of the band at 2,980 cm⁻¹. As shown in Table 2, this suggests that the aliphatic parts in the lignin molecule are the starting point for the thermal decomposition; this included scission of the C-H groups between the adjacent aromatic rings (decrease in the absorption band at wave number 820 cm⁻¹).

The peak of the DTA for the second exothermic reaction is sharp at 380 C at the slow heating rate. The IR spectrum (Fig. 5 and Table 2) of the residue at 380 C shows the disappearance of more absorption bands (1,730, 1,520, 1,470, and 1,230 cm⁻¹). This suggests that, as heating is continued, the thermal decomposition of aromatic rings begins.

The third peak in the DTA curve is at about 450 C. It is probably related to

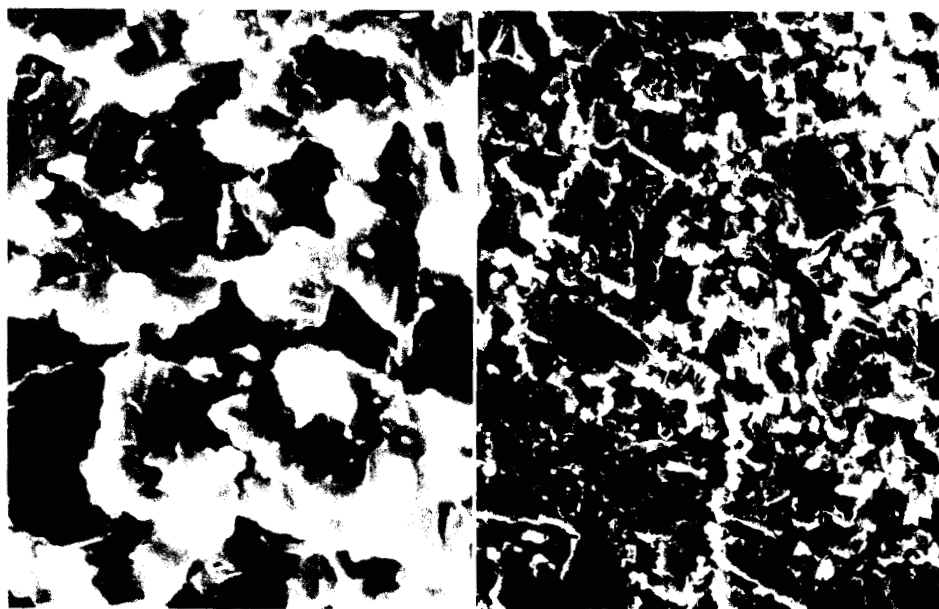


FIG. 6. Scanning electronmicrograph for MWL at room temperature (20 C).

the evolution of hydrogen gas when condensation of the residue carbon in the char into a graphitelike ring occurs (Epremain 1970). The IR spectrum shows that no functional groups have remained except the OH group at wave number $3,400\text{ cm}^{-1}$. New absorption bands appeared at wave numbers $1,540$ and 880 cm^{-1} ,

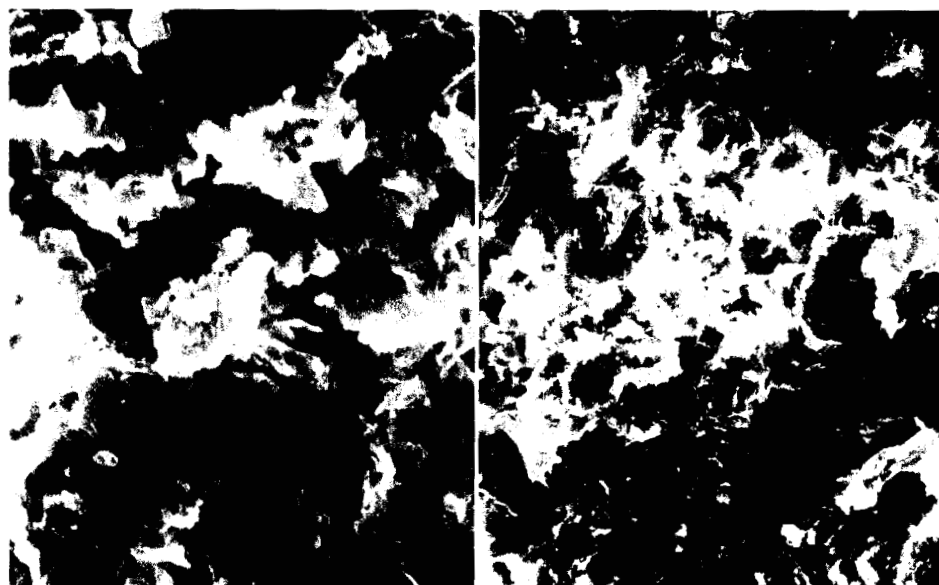


FIG. 7. Scanning electronmicrograph for MWL heated to 190 C.

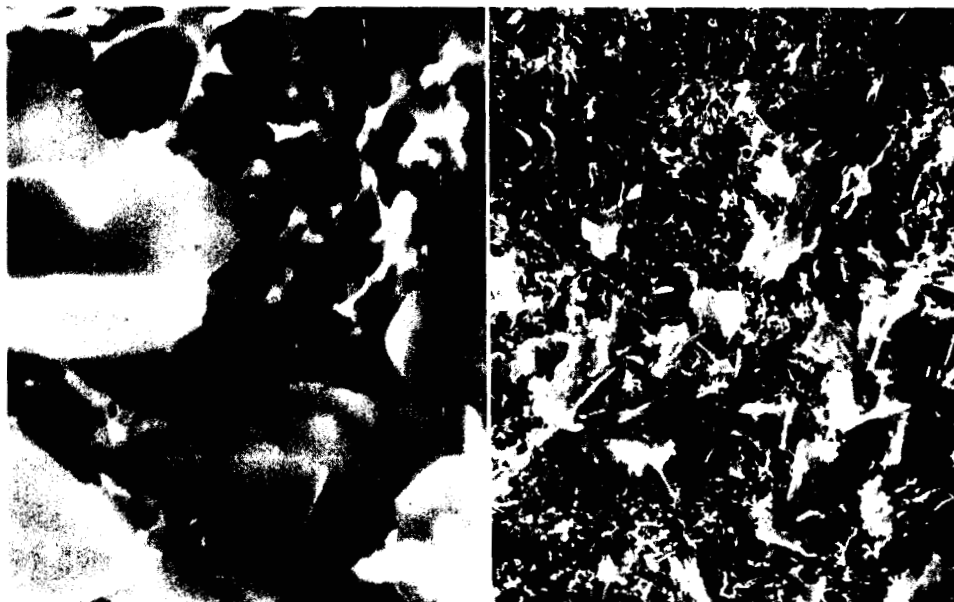


FIG. 8. Scanning electronmicrograph of MWL heated to 280 C.

which are assigned as alkane linkages (Oren et al. 1983); they are probably generated during lignin pyrolysis. The temperatures of the DTA peaks are in good agreement with the findings of Kudo and Yoshida (1957). They found that, on analysis of the methoxyl groups after isothermal heating of dry distilled wood,

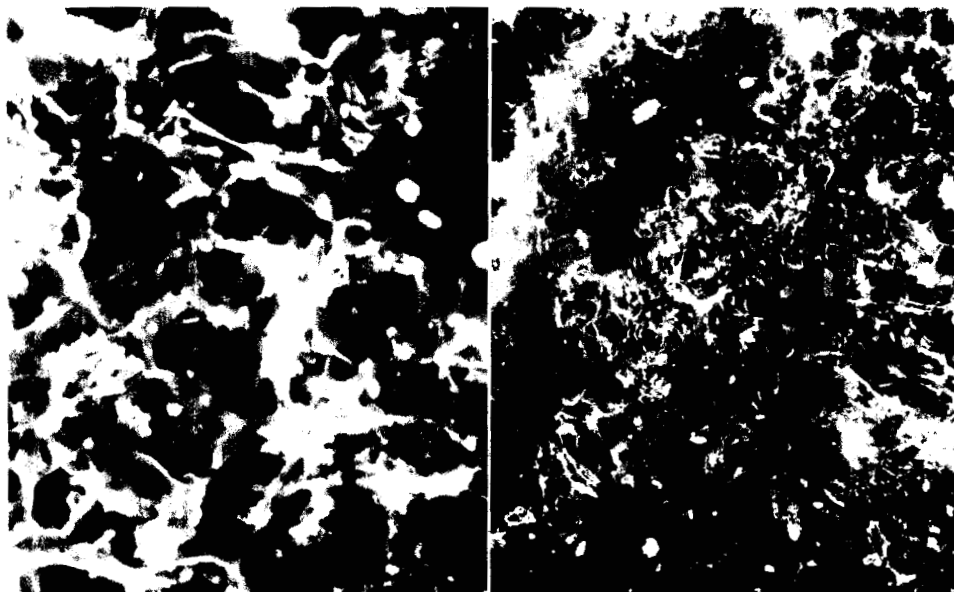


FIG. 9. Scanning electronmicrograph of MWL heated to 380 C.

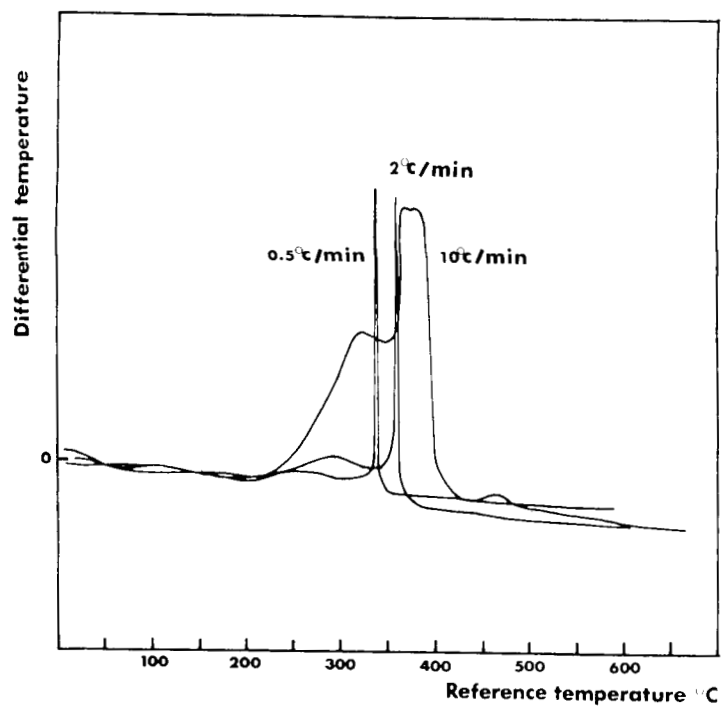


FIG. 10. DTA curves of LCC at different heating rates.

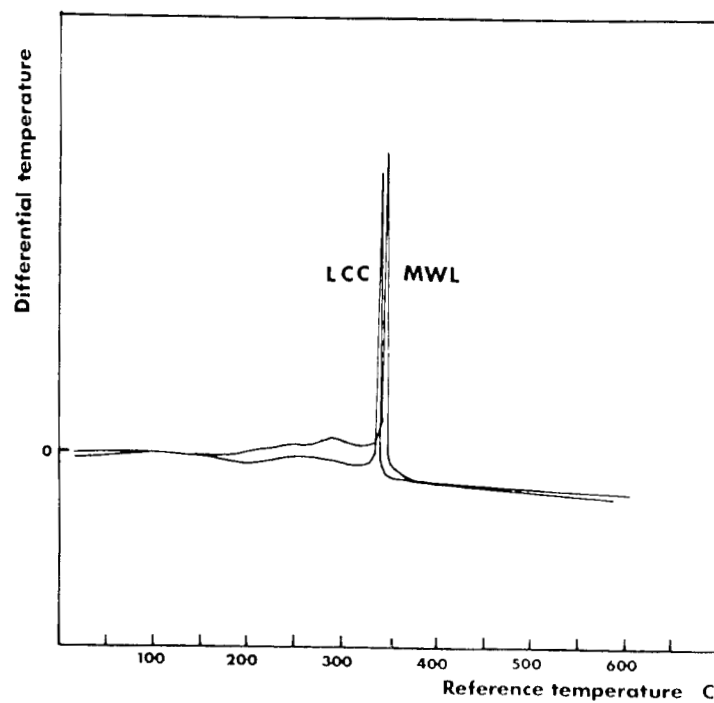


FIG. 11. DTA curve for MWL and LCC at 0.5 C/min.

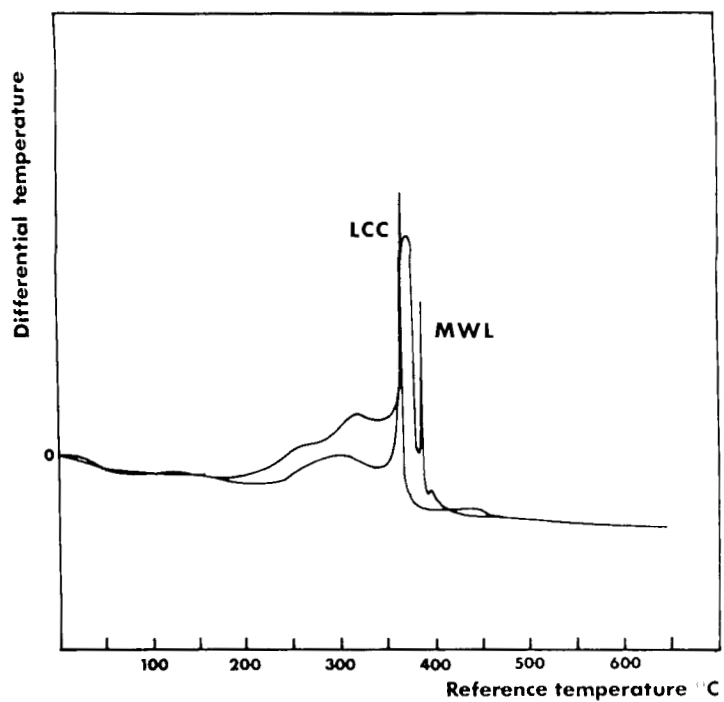


FIG. 12. DTA curve for MWL and LCC at 2 C/min.

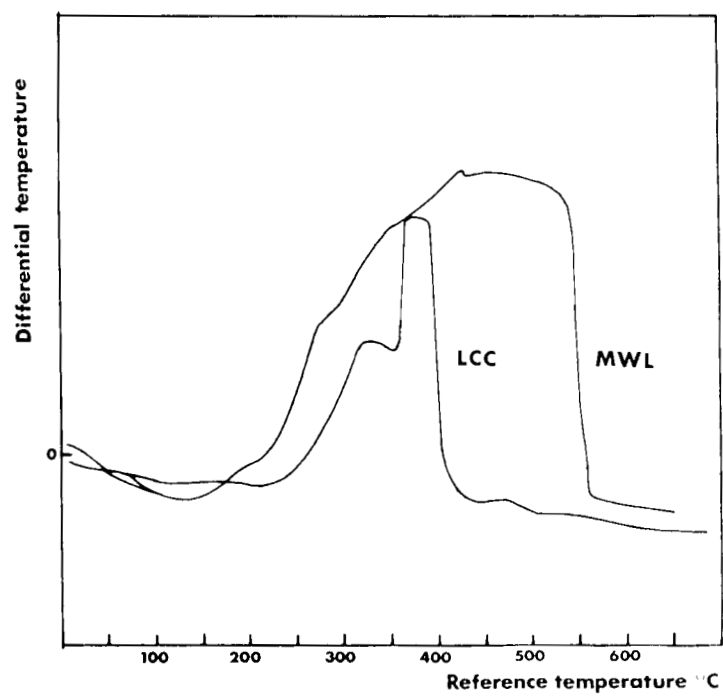


FIG. 13. DTA curve for MWL and LCC at 10 C/min.

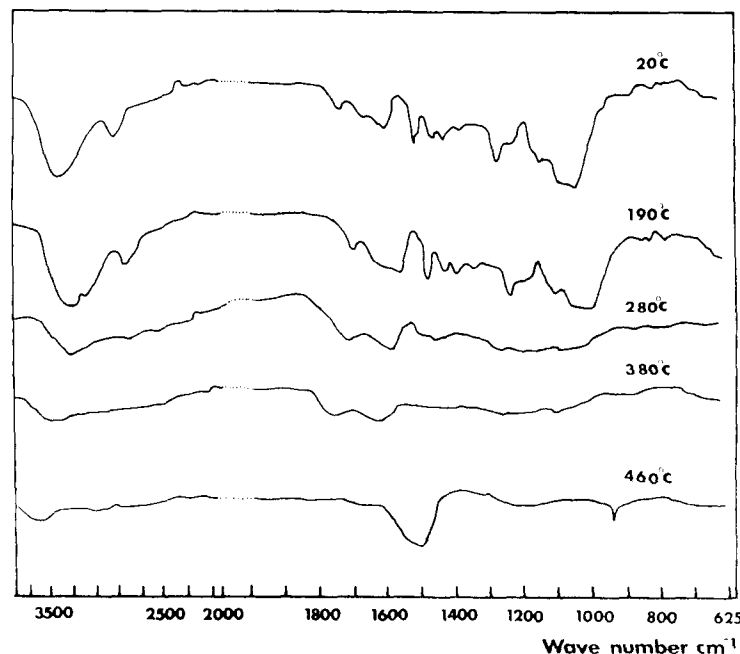


FIG. 14. Infrared analysis of LCC and its pyrolyzed residues.

lignin decomposition begins at about 280 C with a maximum rate occurring between 350 and 450 C and the completion of the reaction at 450 and 500 C. These three temperature ranges correspond to the first, second, and third exothermic peaks found in the present work.

The IR spectrum, Fig. 5, shows that the number of bands was decreased on pyrolysis until the final residue is only carbon. This shows that there is no intermediate compound formed during pyrolysis as there is in the pyrolysis of cellulose (Arseneau 1971): levoglucosan.

Pyrolysis of lignin to carbon is taking place in stages. The scanning micrographs, Figs. 6–9, together with the IR spectrum, Fig. 5, show that the first exothermic peak that appeared at 280 C, attributed to the decomposition of the aliphatic part of the lignin, is accompanied by the extended pyrolysis of some lignin mass to carbon. Patches of carbon first appear at the lignin surface (Fig. 8). The amount of carbon is increased in pyrolysis until it covers the whole lignin surface (Fig. 9). Some lignin particles are probably still present in the interior of the lignin mass and they give rise to the aliphatic bands in the IR spectrum of the 380 C residue (absorption band at wave number $2,980\text{ cm}^{-1}$, Fig. 5). The third exothermic peak in the DTA curve appears when the material is at an advanced stage of carbonization.

If lignin is contaminated with hemicellulose (LCC), the situation for thermal analysis will be as in Fig. 10. The same trend of endothermic and exothermic peaks of MWL is still observed. The endothermic nadir is shifted to a higher temperature as the heating rate is increased. The exothermic peaks are sharp and more pronounced at the slower heating rates. At faster heating rates (10 C/min), the exothermic peaks still retain their identity.

On comparing the DTA curves of the two types of lignin compounds (MWL and LCC) at each heating rate (Figs. 11–13), minor differences can be seen, e.g., the minimum point of the endothermic nadir generally appears at a higher temperature for LCC than for MWL. This is because hemicellulose contains more combined moisture than lignin and the hemicellulose softening point is low compared to lignin. Also, the exothermic peaks of LCC appeared at lower temperature than that of MWL. This is because thermal decomposition of hemicellulose occurs at a lower temperature (Ramiah and Goring 1967).

The similarity between the DTA curves of LCC and MWL may be due to the fact that hemicellulose present in LCC is chemically combined with lignin—hemilignins (Forss et al. 1966). Likewise, the IR spectrum of the LCC (Fig. 14) and that of MWL (Fig. 5) are nearly identical.

This means that the heating rate is the factor that affects the sharpness and position of the exothermic peaks of the DTA curves of lignin.

CONCLUSIONS

1. The endothermic reaction is due to the evolution of moisture, absorbed gases, and the softening of lignin.
2. On pyrolysis of lignin, three successive exothermic reactions occur, the first one at 280 C, where scission of aliphatic groups begins and some lignin on the surface begins to carbonize, the second one at 380 C, where scission of aromatic parts occur and all the lignin on the surface is carbonized. The third one is at 460 C, where the carbon in the char is condensed into graphitelike rings.
3. The heating rate is the factor that determines the sharpness and the position of the exothermic peaks of the DTA curves. The different peaks of the pyrolyzed lignin are well defined at a heating rate of 2 C/min.

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REFERENCES

- ARSENEAU, D. F. 1971. Competitive reactions in the thermal decomposition of cellulose. *Can. J. Chem.* 49(4):632–638.
- BERKOWITZ, N. 1957. The differential thermal analysis of coal. *Fuel* 26:355–373.
- BJORKMAN, A., AND B. PERSON. 1956. The properties of lignin extracted with neutral solvents from soft and hard woods. *Sven. Papperstidn.* 59:477–485.
- BOLKER, H., AND N. G. SOVERVILLE. 1963. Infrared spectroscopy of lignin. *Pulp Pap. Mag. Can.* 164(April):187–193.
- BROWN, F. L. 1958. Theories on the combustion of wood and its control. U.S. Forest Product Lab. Rep. 2136.
- BROWNELL, H. H. 1968. Improved ball milling in the isolation of milled wood lignin. *Tappi* 51(7): 293–300.
- . 1970. Spruce milled wood lignin and lignin-carbohydrate complex. *Tappi* 53(7):1278–1281.
- DOMANSKY, R., AND F. RENDOS. 1962. On the pyrolysis of wood and its component. *Holz Roh-Werkst.* 20:473–476.
- EICKNER, H. W. 1962. Basic research on the pyrolysis and combustion of wood. *For. Prod. J.* 12(4): 194–199.
- EPREMAIN, E. 1970. Thornel, A new graphite reinforcement. *Appl. Polymer Symp.* 15:139–154.

- FORSS, K., K. E. FREMER, AND B. STENLUND. 1966. Spruce lignin and its reaction in sulfite cooking. *Papper O. Tra* 48(9):565–574, II, 669–679.
- HERGERT, H. L. 1960. Infrared spectra of lignin and related compounds. *J. Org. Chem.* 25:405–413.
- KUDO, K., AND E. YOSHIDA. 1957. On the decomposition process of wood constituents in the course of carbonization. *J. Japan Wood Res. Soc.* 3(4):125–127.
- LIANG, C. Y., K. H. BASETT, E. A. MCGINNES, AND R. H. MARCHESAULT. 1960. Infrared spectra of crystalline polysaccharides. *Tappi* 43(12):1017–1024.
- OREN, J. J., M. M. NASSAR, AND G. D. M. MACKAY. 1983. Infrared study of inter-carbonization of spruce wood lignin. Submitted to *Can. J. Spectroscopy*.
- PEARL, I. A., AND L. R. BUSCHE. 1960. Studies on the chemistry of aspen wood. *Tappi* 43(12):960–969.
- PILICHUK, YU. S., R. Z. PEN, A. V. FINKEL'SHTEIN, AND I. L. SHAPIRO. 1966. Infrared spectroscopic study of lignin. *Izv. Vyssh. Ucheb. Zavad., Les. ZH* 9(6):116–118, CF., CA., 66:96365J.
- RAMIAH, N. V., AND D. A. I. GORING. 1967. Some dilatometric measurements of the thermal decomposition of cellulose, hemicellulose and lignin. *Cell. Chem. Technol. (Jassy)* 1(3):277–285.
- SANDERMANN, W., AND H. AUGUSTIN. 1963. Chemical investigations of thermal decomposition of wood. *Holz Roh-Werkst.* 12:256–268.
- , AND ———. 1964. Chemical investigations on the decomposition of wood. *Holz Roh-Werkst.* 22:377–386.
- SARKANEN, K. V., HOU-MIN CHANG, AND B. ERICSSON. 1967. Species variation in lignin. *Tappi* 50(11):572–575.
- STAMM, A. J. 1962. Thermal degradation of wood and cellulose. *Ind. Eng. Chem.* 48:413–417.
- TANG, W. K. 1967. Effect of inorganic salts on pyrolysis of wood, cellulose, and lignin determined by dynamic thermogravimetric. USDA Forest Service Research Paper FPL71.
- , AND H. W. EICKNER. 1968. Effect of inorganic salts on pyrolysis of wood, cellulose and lignin by DTA. USDA Forest Service Research Paper FPL82.
- , AND W. K. NEILL. 1964. Effect of flame retardants on pyrolysis and combustion of alpha-cellulose. *J. Polymer Sci.* 6:65–81.