STUDIES ON THE MECHANISM OF FLAME RETARDATION IN WOOD

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ABSTRACT

Two lignins, of different carbohydrate content, were pyrolyzed before and after treatment with inorganic salts. Lignin that is relatively free of carbohydrate was inert to the salts: its DTA curve did not change. The DTA curve of lignin associated with about 50% carbohydrate showed a shift of the exothermic peak to a higher temperature and the appearance of a new exotherm; lithium chloride was the most effective salt in causing this shift. The results support the chemical theory of flame retardation.

Keywords: Inorganic salts, flame retardation, pyrolysis, wood combustion.

INTRODUCTION

The combustion of wood is an important area of fire research. The effect of inorganic salts on the combustion process is of practical interest both for their fire retardant action and for their value in the elucidation of the combustion process.

Several theories of fire retardation have been advanced (Browne 1958; Little 1947; Tyner 1941). These theories are based on different concepts: dilution of combustible gases with noncombustible gases, thermal conduction of heat away from the flame front, coating of the combustible substrate to prevent oxidation, and modification of the decomposition process (the so-called "Levoglucosan theory").

The Levoglucosan theory has been studied (Parks et al. 1955; Schwenker and Pacsu 1958). It is suggested that, during the pyrolysis of cellulose, the rate determining step is depolymerization to form a flammable intermediate, levoglucosan. It is proposed that chemicals which inhibit the formation of levoglucosan retard the flaming combustion of wood.

Thermal degradation of lignin treated with inorganic salts has been studied extensively by Tang and Eickner (1968). However, they used sulfuric acid lignin, which is usually degraded during preparation. In the present work, two types of lignin were used, prepared under very mild conditions (Brownell 1968; 1970) to prevent lignin degradation. One type is free from carbohydrate (Brownell 1968), while the other contains about 50% carbohydrate (Brownell 1970). The aim of the present work is to examine during pyrolysis the effect of salts on the lignin free from carbohydrate and on a lignin carbohydrate complex.

EXPERIMENTAL

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

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TABLE 1.   *Lignin content of samples isolated from black spruce woods.* *

Sample	Klason lignin	Weight of klason lignin as % of total klason lignin in wood	Milling procedure
MWL	90.01[a]	28.7	3 weeks ball-milled. Milled air-dry with flint pebbles.
LCC	56.71[b]	24.1	3 weeks ball-milled. Milled dry under N_2 with small Burundum cylinders.

* West K. Forintek Canada Corp., Chemistry section.
[a] Essentially free from carbohydrate (Brownell 1968).
[b] It is composed of single molecules of hemicellulose of DP 18 linked to single molecules of lignin (Brownell 1970).

Thermograms were obtained using a CSI Stano Premco Model 202 differential thermal analyzer (DTA) with temperature programmed at 5 C/min. heating rate, from room temperature to 700 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 was 18 mg; the reference material was aluminum oxide.

Lignin was treated by soaking the samples in a 2% aqueous solution of the salt under vacuum. The vacuum was maintained for 20 min; the lignin slurry was then air dried. The gain in weight of the specimens after treatment was about 2% for all salts.
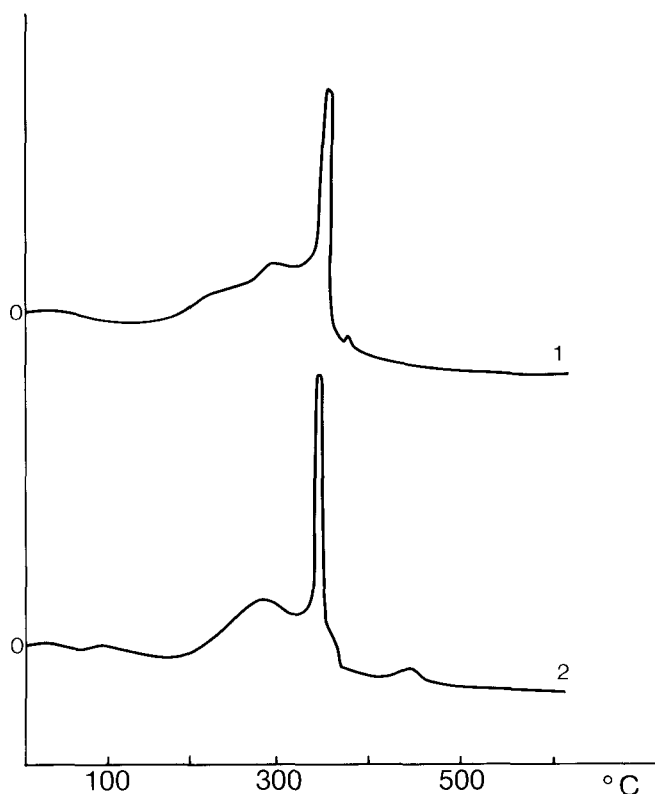

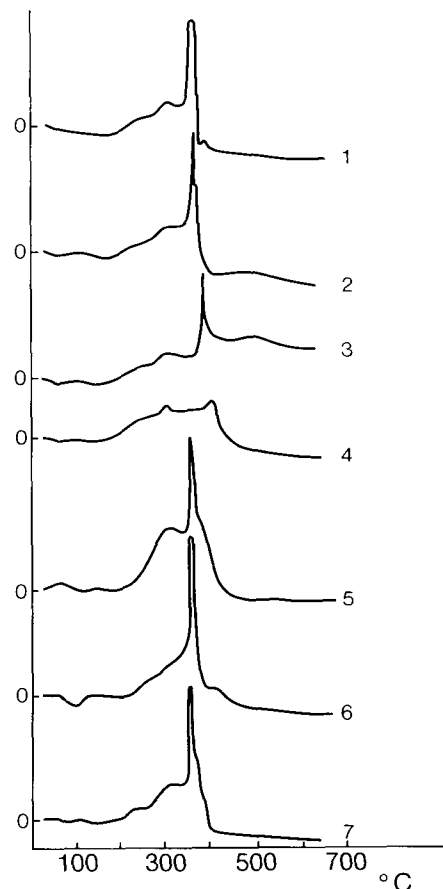FIG. 1.   DTA thermograms of MWL (1) and LCC (2) at inert atmosphere.

FIG. 2. (1) LCC, (2) sodium tetraborate, (3) aluminum chloride, (4) ammonium phosphate, (5) lithium chloride, (6) potassium bicarbonate, (7) calcium chloride.

DISCUSSION

Comparison of the DTA curves of the two types of lignin shows a strong similarity up to a temperature of 350 C. At a temperature of 400 C, a peak appeared for LCC but not for MWL. The peak can be attributed to the presence of carbohydrate in LCC (Table 1). The presence of carbohydrate during pyrolysis of lignin can shift the exothermic peak to a higher temperature (Arseneau 1961). On pyrolysis of carbohydrate (cellulose), depolymerization occurs and the product escapes as tar. Levoglucosan is an essential intermediate in this step (Schwenker and Pacsu 1958).

The effect of salts on the two types of lignin is shown in Figs. 2 and 3. Comparison shows that salts have no effect on MWL. This finding differs from that of Tang and Eickner (1968); they reported that the endothermic and the exothermic reactions of lignin are modified to varying degrees by inorganic salts. In previous work done in this lab (Nassar and MacKay 1983), it was shown that MWL degrades thermally to carbon without a distinct intermediate.

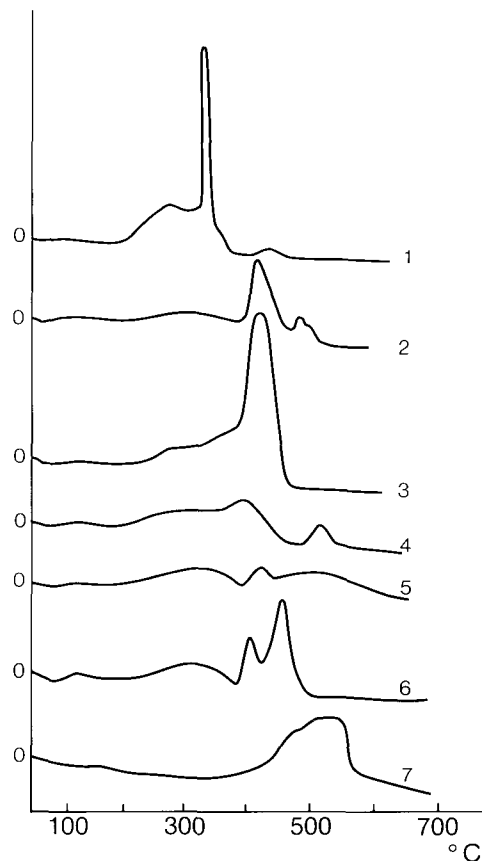On the other hand, the DTA peaks from pyrolysis of LCC are modified with

FIG. 3. (1) MWL, (2) sodium tetraborate, (3) aluminum chloride, (4) ammonium phosphate, (5) lithium chloride, (6) potassium bicarbonate, (7) calcium chloride.

addition of 2% of inorganic salts as shown in Fig. 3. All peaks have been shifted to a higher temperature of 400 to 500 C. In the case of sodium borate, the exothermic peak was shifted to 450 C and a second exothermic peak appeared at 510 C. With aluminum chloride, the exothermic peak shifted to 450 C. Potassium bicarbonate reduced the intensity of the exothermic peak and divided it into two moderate exothermic peaks with a weak endotherm intervening. Calcium chloride treatment gives one broad exothermic peak (between 420–500 C). Ammonium phosphate and lithium chloride cause a shifting of the exothermic peak to 400 and 420 C, respectively, and the appearance of a second exothermic peak at 520 C. Ammonium phosphate and lithium chloride cause the greatest reduction in exothermic peaks; lithium chloride was the most effective.

CONCLUSION

The intensity and the position of the exothermic DTA peaks from LCC vary under the influence of inorganic salts. The salts do not affect the DTA peaks of MWL, which is free of carbohydrate. The results indicate that pyrolysis of lignin is inert to inorganic salts, while pyrolysis of carbohydrate is affected by the salts.

In respect to flame-retardant theories, the results can be explained based on chemical reaction theory; the salts only modify the active component of wood, namely carbohydrate.

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