Thermochimica Acta, 81 (1984) 9–14
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

STUDIES ON THE MECHANISM OF FLAME RETARDING

MAMDOUH M. NASSAR * and G.D.M. MACKAY

Centre for Energy Studies and Department of Chemical Engineering, Technical University of Nova Scotia, Halifax, Nova Scotia (Canada)

(Received 11 May 1984)

ABSTRACT

Two lignins, of different carbohydrate content, were pyrolysed before and after treatment with inorganic salts. Lignin, which 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. The results support the chemical theory of flame retardation.

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 for their fire retardant action and for their value in the elucidation of the combustion process.

Several theories of fire retardation have been advanced [1–3]. These theories are based on different concepts: dilution of combustible gases with non-combustible 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 [4,5]. It is suggested that, during 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.

Extensive thermal studies on lignin treated with inorganic salts have been made by Tang and Eickner [9], however, they used sulfuric acid lignin which is usually degraded during preparation. In the present work two types of lignin were used. They were prepared under very mild conditions [6,7] to

---

* Permanent address: Faculty of Engineering, Minia University, El Minia, Egypt.

prevent lignin degradation. One type is carbohydrate free [6], while the other contains about 50% carbohydrate [7]. The aim of the present work is to study the effect of salts on the two types of lignin, during pyrolysis, and consequently to show the role of inorganic salts on the thermal characteristics of lignin.

EXPERIMENTAL

The lignin samples used were milled wood lignin (MWL) and lignin carbohydrate complex (LCC) from black spruce [6,7].

Thermograms were obtained using a CSI Stano Premco Model 202 differential thermal analyzer (DTA) with temperature programmed at 5 °C min^{-1} 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 ft.^3 h^{-1} 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 salts under vacuum. The vacuum was maintained for 20 min; the lignin slurry was then air dired. The gain in weight of the specimens after treatment was about 2% for all salts.

DISCUSSION

Comparison of the DTA curves of the two types of lignin shows a strong similarity up to a temperature of 350 °C (Fig. 1). At a temperature of 400 °C, a peak appeared for LCC but not for MWL. This peak can be attributed to the presence of carbohydrate in LCC (Table 1). The presence of carbohydrate during the pyrolysis of lignin can shift the exothermic peak to a higher temperature [8]. On pyrolysis of carbohydrate (cellulose), depolymerization occurs and products escape as tar; work [5] has shown that levoglucosan is an essential intermediate in this step.

The effect of salts on the two types of lignin are shown in Figs. 2 and 3. Comparison of the results revealed that salts have no effect on MWL. This finding is different to that of Tang and Eickner [9] who reported that the endothermic and exothermic reactions of lignin are modified to different degrees by inorganic salts. In previous work done in this laboratory [10], it was shown that, on thermal decomposition, MWL degrades to carbon without any distinct intermediate.

On the other hand, the LCC pyrolysis DTA peaks are modified by the addition of 2% of the various inorganic salts, as shown in Fig. 3. All peaks have been shifted to the higher temperature of 400–500 °C. In the case of sodium borate the exothermic peak was shifted to 450 °C and a second

TABLE 1

Lignin content of samples isolated from black spruce wood [a]

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

[a] West K. Forintek Canada Corp., Chemistry section.

[b] Essentially free from carbohydrate [6].

[c] It comprised single molecules of hemicellulose of DP 18 linked to single molecules of lignin [7].

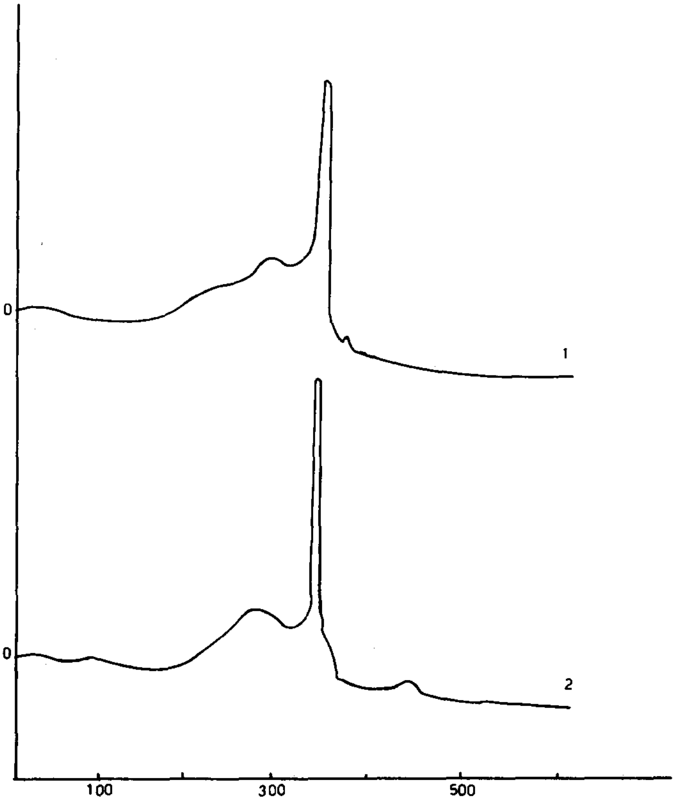

Fig. 1. DTA thermograms of MWL (1) and LCC (2) in inert atmosphere.

exothermic peak appeared at 510 °C. With aluminum chloride the exothermic peak shifts to 450 °C. Potassium bicarbonate reduced the intensity of the exothermic peak and divided it into two moderate exothermic peaks with a weak endothermic peak interrupting the exotherms. Calcium chloride gave a broad exothermic peak (420–500 °C) covering the two exothermic peaks. Ammonium phosphate and lithium chloride showed a shifting of the exothermic peak to 400 and 420 °C, respectively, and the appearance of a second exothermic peak at 520 °C. However, ammonium phosphate and lithium chloride caused the greatest reduction of all heat intensities, lithium chloride being the most effective.

CONCLUSION

The intensity and the position of the exothermic peaks of LCC varied according to the effect of the type of each salt on the carbohydrate

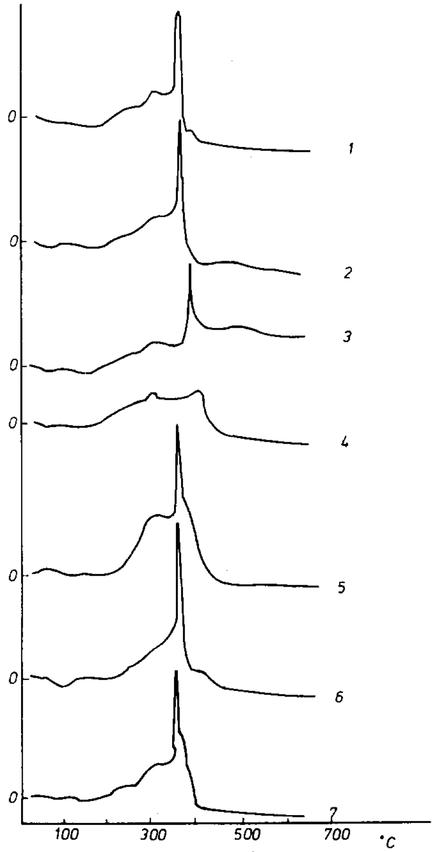

Fig. 2. DTA thermograms of MWL and MWL treated with salts: (1) MWL; (2) sodium tetraborate; (3) aluminum chloride; (4) ammonium phosphate; (5) lithium chloride; (6) potassium bicarbonate; (7) calcium chloride.

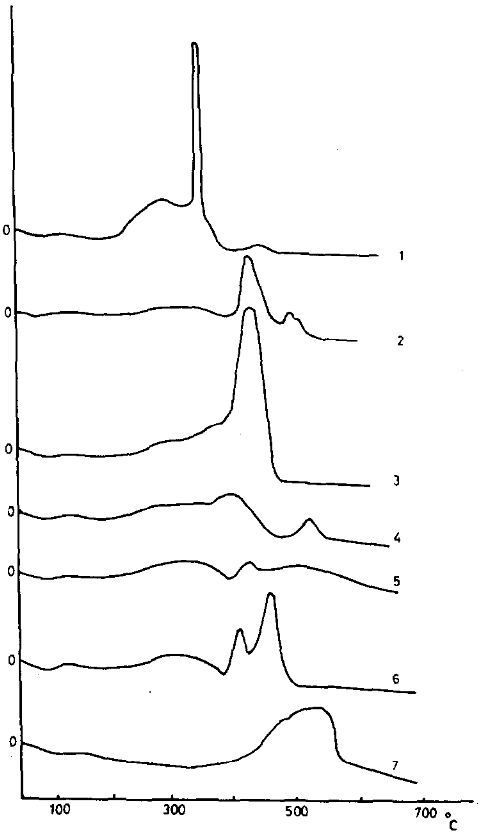

Fig. 3. DTA thermograms of LCC and LCC treated with salts: (1) LCC; (2) sodium tetraborate; (3) aluminum chloride; (4) ammonium phosphate; (5) lithium chloride; (6) potassium bicarbonate; (7) calcium chloride.

associated with the lignin. Since such an effect did not appear in MWL, which is relatively free of carbohydrate, this suggests that lignin behaves as an inert material with respect to the action of the salts, while carbohydrate is chemically modified by the salts during pyrolysis, causing changes in thermal characteristics as shown in the DTA curves. This finding can, therefore, be considered to support the chemical reaction theory of flame retardation.

REFERENCES

1 F.L. Browne, Theories of the combustion of wood and its control, Rep. 2136, USDA Forest Service, Forest Prod. Lab., Madison, WI, 1958.

2 R.W. Little, Flame Proofing of Textile Fabrics, Reinhold, New York, 1947.

3 H.D. Tyner, Ind. Eng. Chem., 33 (1941) 60.

4 W.G. Parks, R.M. Esteve, Jr., M.H. Gollis, R. Guercia and A. Petrarca, Mechanism of the pyrolytic decomposition of cellulose, Pap. 15, Div. Cellulose Chem. Abstracts, 127th ACS Meet., Cincinnati, OH, 1955, p. 70.

5 R.F. Schwenker, Jr. and E. Pacsu, Ind. Eng. Chem., 50 (1958) 91.
6 H.H. Brownell, Tappi, 51 (1968) 298.
7 H.H. Brownell, Tappi, 58 (1970) 1278.
8 D.F. Arseneau, Can. J. Chem., 39 (1961) 1915.
9 W.K. Tang and H.W. Eickner, Effect of inorganic salts on pyrolysis of wood, cellulose and lignin determined by DTA, U.S. Forest Service, Res. Pap. FPL82.
10 M.M. Nassar and G.D.M. MacKay, Wood Fiber Sci., 16 (1984) 441.