

## NOTE

# PYROLYSIS PRODUCTS OF *PINUS CONTORTA* BARK

T. D. LOMAX and R. A. FRANICH

Ministry of Forestry, Forest Research Institute, Private Bag 3020,  
Rotorua, New Zealand

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### ABSTRACT

The yields of char, tar, and non-condensable gases from the pyrolysis of *Pinus contorta* Loudon bark were measured. The major components of the pyrolysis tar (5.5% yield) were catechol and 2-methyl catechol. Pyrolysis gave 45% char with ash content 3.5% (mainly aluminium, calcium, potassium, and silica).

**Keywords:** bark; pyrolysis; phenolics; *Pinus contorta*.

### INTRODUCTION

Using wood as a source of chemicals (to replace fossil fuels) is a well-recognised concept (Emsley 1987). Although wattle tannins and phenolic modified pine tannins have been used as wood adhesives (Pizzi 1983) and some other industrial uses have been found (Roux *et al.* 1975), the use of bark as a similar resource has received rather less attention.

Bark contains a high percentage of tannins and related phenolic compounds (Markham & Porter 1973). It is available in large quantities (about 10% of the yield of milled timber), largely as a waste material, and is primarily disposed of as fuel.

Pyrolysis of lignocellulosic biomass produces, amongst other compounds, a complex mixture of phenolic compounds which are derived primarily from the lignin fraction of the biomass (Thring *et al.* 1989). The pyrolysis of wood for phenolic adhesives is currently of interest (Chum *et al.* 1989). Previous study of the pyrolysis of bark was concentrated largely on its potential for gas production (Kumar & Mann 1982), and there is little information on the constituents of the pyrolysis tars derived from such processes. *Pinus contorta* bark is available only in small quantities in New Zealand (4428 ha *P. contorta* plantations v. 1 108 283 ha *P. radiata* D. Don (A. Bell, Crown Forest Asset Sales Group, pers. comm.; Turland & Novis 1990), and can occur as a contaminant in bark from *P. radiata* origin. The trial described in this paper was carried out to investigate the pyrolysis products of *P. contorta* bark.

### METHODS

*Pinus contorta* bark was obtained from the industrial debarker at Fletcher Wood Panels Ltd, Taupo, New Zealand.

## Pyrolysis

### *Preparative pyrolysis*

For this method of pyrolysis, 6.68 g bark at 13.6% moisture content was placed in a round-bottomed flask, purged with nitrogen, and pyrolysed at atmospheric pressure using an air/acetylene flame. The condensed tar was collected and extracted with diethyl ether. The ether layer was dried over sodium sulphate, filtered, and concentrated under reduced pressure, and the weight of residue was determined.

### *Analytical pyrolysis*

In the second method small samples (approx 1 mg) of powdered air-dry bark were placed into quartz pyrolysis tubes, inserted into a platinum coil-type pyrolyser probe and into a pyrolysis oven held at 200°C, purged with helium for 1 min, and heated ballistically to 650°C for 20 s. The pyrolysate was transferred to an analytical gas chromatograph (GC) column using a helium flow rate of 1 ml/min. After 1 min the pyrolysis oven and injector were purged by increasing the helium flow to 20 ml/min.

## Chromatography

### *Gas chromatography and mass spectrometry conditions*

Fused silica open tubular capillary column 25 m x 0.2 mm, Carbowax 20 M phase. Injector temperature 220°C. Flame ionisation detector temperature 250°C. Initial oven temperature 50°C. Initial time 2 min. Rate 4°C/min. Final temperature 190°C. Final time 40 min. The gas chromatograph mass spectrometer was operated in electron ionisation mode. Ion source temperature 200°C. Electron energy 70 eV, 300 µA.

### *Column chromatography of isolated tar*

A portion of the tar was chromatographed on a silica column which was progressively eluted with hexane, hexane/dichloromethane 9:1, 4:1, and 1:1, dichloromethane, dichloromethane/ethylacetate 9:1 and 1:1, ethylacetate, methanol, water, and water/acetic acid 9:1. The weight of each fraction was recorded. The isolated fractions were analysed by thin-layer chromatography using silicagel GF254 plates.

### *Infrared and proton NMR spectrometry*

Infrared spectra were recorded in chloroform using 0.1 mm sodium chloride cells on a Digilab Fourier transform infrared spectrometer. Proton NMR spectra were analysed using a Bruker AC200 spectrometer operating at 60 MHz.

## Non-condensable Gas Determination

For determining the volume of non-condensable gases a sample of 1 g bark was pyrolysed and compared with the volume from a blank run. The gas sample was left for 12 h before the volume was measured, and 250 µl gas was analysed by gas chromatography using a Porapak Q column at 83°C with helium gas carrier (28 psi, 22 ml/min) and thermal conductivity detector.

## Elemental Analysis of Bark Pyrolysis Char

The pyrolysis char was heated at 600°C for 4 h for determination of ash content. The ash was analysed by energy dispersive X-ray analysis (EDX) of six spot samples for an estimate of its constituents.

## RESULTS AND CONCLUSIONS

The preparative pyrolysis of *P. contorta* bark yielded 5.5% ether extractives, 45% char, and 133 ml gas comprising 13.5% methane and 86.5% carbon dioxide. The ash content of the char was found to be 3.5% (Table 1).

TABLE 1—Analysis of inorganic constituents of char from pyrolysis of *Pinus contorta* bark.

|            | Area (%) of<br>detected elements |
|------------|----------------------------------|
| Silica     | 7.3                              |
| Calcium    | 44.3                             |
| Aluminium  | 20.9                             |
| Iron       | 4.4                              |
| Potassium  | 10.0                             |
| Chlorine   | 5.7                              |
| Titanium   | 0.8                              |
| Sulphur    | 1.6                              |
| Phosphorus | 1.7                              |
| Magnesium  | 3.4                              |

Approximately 70 significant peaks were observed in the GC and GCMS chromatograms of the pyrolysate obtained by the analytical pyrolysis. The GCMS retention times, the area percentage obtained from the GC data, and the total ion chromatography / mass spectral peak identity where we have been able to identify the compound for a given peak are listed in Table 2.

Our results show that significant quantities of catechol and closely related compounds are available from pyrolysis of bark. The fraction from column chromatography which contained catechol and methylcatechols could be readily purified and obtained as a dark semi-crystalline material. It is evident that some highly polar or high molecular weight compounds failed to elute from the column and were therefore not analysed. Main uses for catechol are in manufacture of photographic developers, tire adhesives, antioxidants, inhibitors, insecticides, wood adhesives, UV absorbers, and dye stuffs. The pyrolysis products from wood material have been developed as adhesives (Chum *et al.* 1989) and the level of catechol and other phenolics in the pyrolysis tars from *P. contorta* bark would suggest similar possibilities. As bark in general contains less water than wood, and is available in large quantities as a waste material, pyrolysis of bark for adhesive raw materials may well be economically and environmentally more useful than pyrolysis of wood for a similar end-use.

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TABLE 2—Compounds identified from the pyrolysis of *Pinus contorta* bark under an inert atmosphere, as measured by total ion GCMS and flame ionisation GC (FID) on raw bark samples.

| Total ion retention time (min) | Identity (by mass spectrum)      | Area (%) (uncorrected for FID response factor) |
|--------------------------------|----------------------------------|--|
| 11.2                           | Furfural                         | 3.34   |
| 18.2                           | Naphthalene                      | 2.17   |
| 21.5                           |                                  |  |
| 21.9                           | Acetylcyclohex-1-ene             | 6.72   |
| 22.1                           | Unknown                          | 4.23   |
| 24.3                           | Unknown, m/z 138                 | 2.47   |
| 25.6                           | Phenol plus unknown              | 1.74<br>1.49                                   |
| 26.2                           | 2,4-dihydroxyacetophenone        |  |
| 27.6                           | 2-methylphenol                   | 1.05   |
| 27.7                           | 4-methylphenol                   | 0.87   |
| 29.6                           | Biphenylene                      | 0.8  |
| 29.7                           | 2-ethylphenol                    | 4.67   |
| 30.1                           | Unknown, m/z 150                 | 2.88   |
| 33.5                           | Isoeugenol                       | 1.31   |
| 33.6                           | Eugenol                          | 3.25   |
| 34.3                           | 2,3-dihydrobenzofuran            | 1.28   |
| 36.1                           | Unknown                          | 0.97   |
| 37.0                           | Hydroxymethylfurfural            | 1.23   |
| 37.1                           | 3,4-dimethylbenzaldehyde         | 2.27   |
| 38.1                           | 3-methoxy-4-hydroxybenzaldehyde  | 0.89   |
| 38.5                           | Unknown                          | 2.14   |
| 39.7                           | 3-methoxy-4-hydroxy-acetophenone |  |
| 40.1                           | Unknown, m/z 272                 | 2.30   |
| 40.2                           | 3-methylcatechol                 | 1.09   |
| 40.8                           | Catechol                         | 17.78  |

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