NOTE

PYROLYSIS PRODUCTS OF *PINUS RADIATA* BARK

T. D. LOMAX, R. A. FRANICH, and H. KROESE

Forest Research Institute, Private Bag 3020, Rotorua, New Zealand

(Received for publication 9 October 1991; revision 11 December 1991)

ABSTRACT

The yields of char, tar, and non-condensible gases from the pyrolysis of *Pinus radiata* D. Don bark were measured. Pyrolysis of bark, on a small preparative scale using an air-acetylene flame, gave 48% char with ash content 3.5% (mainly aluminium, calcium, potassium, and silica), and recovered tar in 7% yield (on oven-dried bark equivalent). The major components of the pyrolysis tar were catechol and 2-methyl-catechol.

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

INTRODUCTION

The volume of pine bark produced in New Zealand is considerable. Annual pine log production is currently about 13 000 000 m^3 and is projected to increase to about 30 000 000 m^3 by the year 2000. Of the current harvest about 2 000 000 m^3 is exported as unbarked logs. Bark production in New Zealand is therefore estimated at about 7% of 11 000 000 m^3, or about 800 000 m^3, and by 1995 will be about 1 000 000 m^3 (van Wyk 1990). As bark is largely a waste material, economic uses for this large resource are being sought and pyrolysis for phenolic compounds is an option. *Pinus radiata* bark contains a high percentage of tannins and related polyphenolic compounds (Markham & Porter 1973) which are converted to simple phenolic compounds on pyrolysis.

A study of *Pinus contorta* L. bark (Lomax & Franich 1990) showed that catechol and closely related chemicals are potentially available in large supply via pyrolysis. Study in the United States on the pyrolysis of wood for phenolics (Anon. 1989) indicated that waste wood can produce phenolics at a price competitive with petroleum-based supplies. The study described here was carried out to investigate the pyrolysis products of *P. radiata* bark.

METHODS

Pinus radiata bark was obtained from Fletcher Wood Panels, Taupo, and from butt logs of 25- to 28-year-old trees grown in Kaingaroa Forest and debarked at the Mamaku Sawmill near Rotorua.

The methods used in the pyrolysis and in the gas chromatography and the gas chromatography/mass spectrometry (GCMS) analyses have been described previously (Lomax & Franich 1990). Analytical pyrolysis was carried out as before, with minor changes to injection technique and column choice. An improved separation of the pyrolysate was obtained with a Supelco Wax 10 Column. The pyrolysis-oven in the GCMS instrument was purged with 40 ml helium/min before sample introduction. The pyro-oven was then closed and when column head pressure reached 83 kPa pyrolysis was commenced and the mass spectrometer started. Helium flow was dropped to 5 ml/min for 1.5 minutes, then increased to 25 ml/min to simulate purged/splitless injection. Final column temperature of 250°C was maintained until the pyrogram was finished. All other conditions were maintained as in the previous study (Lomax & Franich 1990).

RESULTS AND DISCUSSION

The results from the GC and GCMS chromatograms indicate that pyrolysis of *P. radiata* bark produces chemical compounds similar to those observed in the pyrolysate from *P. contorta* bark (Lomax & Franich 1990). Flame ionisation detector GC (FID/GC) retention times, the percentage area obtained from the GC data, and the identity of the compounds obtained from the total ion chromatogram mass spectral analysis are listed in Table 1. The major difference between the products of pyrolysis of *P. contorta* and *P. radiata* barks appears to be in the relative proportions of the major components rather than the nature of the components, although the observed levels are dependent upon pyrolysis temperature and factors such as moisture content and particle size.

A difference in composition of the pyrolysate was observed with increasing pyrolysis temperature. Previous studies on wood pyrolysis (Donnot *et al.* 1985; Kumar & Mann 1982) indicated that an increase in non-condensible gases at the expense of char was to be expected with increasing temperature. We also observed a change in yield of catechol with increasing temperature (Table 1). The yield of catechol increased from 1.3% at 505°C to over 8% of the FID observable pyrolysis products at 840°C, or from 2.7% to over 15% of the condensible gases at the highest temperatures measured.

The preparative pyrolysis of *P. radiata* bark yielded 7% diethyl ether extractives, 48% char, 1.3% methane, and 5% carbon dioxide. Results from the preparative pyrolysis showed that catechol can be isolated along with methyl catechol by column chromatography (Fig. 1). As the tannins and related flavonoids are a major constituent of barks, it is presumed that the catechol arises by pyrolysis of the tannin β ring. The balance of the major chemicals observed is listed in Table 1 and illustrated in Fig. 2 as components of the pyrolysate from bark at a pyrolysis temperature of 840°C. The presence of ethyl phenols and eugenol in pyrolysis products of bark from both *P. radiata* and *P. contorta* is indicative that lignin is present in these barks and is the first reported evidence supporting the assumption (Uprichard 1991) that lignin accounts for some 15% of the weight of *P. radiata* bark.

TABLE 1–Main components of condensible gases from pyrolysis of *Pinus radiata* bark

FID GC elution time	Most likely chemical identity	Pyrolysis temperature (°C)					
		840	820	795	740	660	505
17.1	furfural	7.1	6.6	10.7	5.4	8.8	16.8
17.2	2-methoxy, 3-methyl tetrahydrofuran	6.3	5.2	5.2	2.6	–	6.8
20.8	5-methylfurfural						
29.0	2- or 4-methoxyphenol	4.4	4.2	6.5	8.2	9.8	4.4
31.6	2-methoxy-4-methylphenol	4.0	3.7	5.2	6.9	10.0	1.5
32.9	2-methoxy-4-ethylphenol	8.3	10.1	12.3	7.3	7.3	2.6
34.9	phenol plus	3.1	4.0	4.9	3.5	3.5	0.0
35.1	methyl phenol	2.5	3.0	3.6	2.6	2.0	0.0
37.0	3-ethylphenol						
37.8	2-hydroxy-5-methyl phenol	4.8	5.0	7.0	9.0	10.0	9.3
41.3	5-hydroxymethyl furfural	1.7	1.6	2.5	2.7	3.7	4.5
44.8		1.6	1.4	3.2	1.7	2.7	2.0
49.0	catechol	15.3	9.0	10.3	11.9	11.2	2.7
53.4	2,3-dihydroxy methyl catechol	0.3	0.6	0.7	0.9	1.2	5.8
59.9						5.8	
Balance of GC peaks		40.6	45.6	27.9	37.7	29.8	37.8

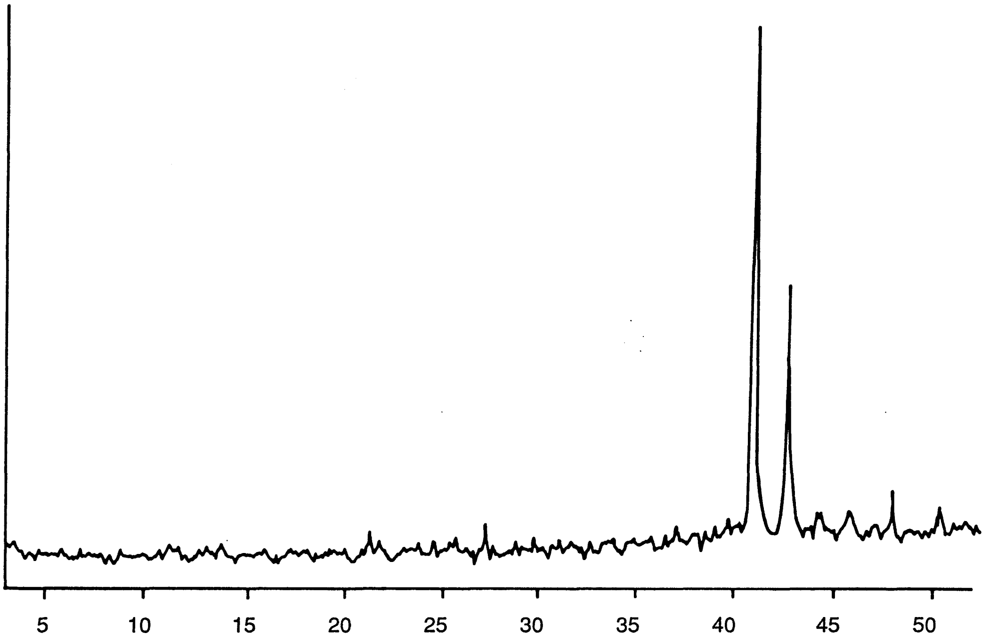

FIG. 1–Total ion chromatogram of catechol fraction from tar of pyrolysed *Pinus radiata* bark separated on a silica column, showing predominance of two components—catechol and methyl catechol.

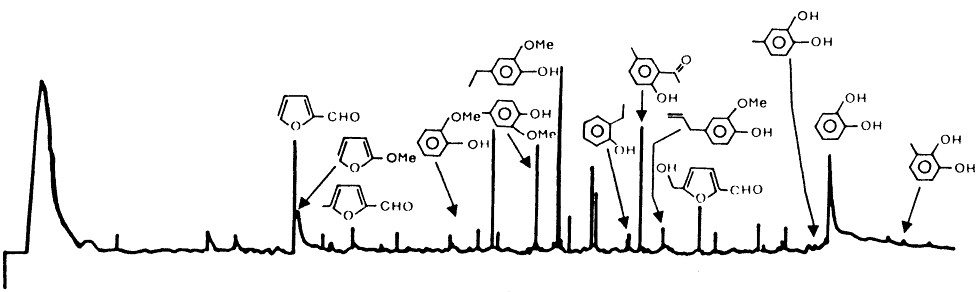

FIG. 2–FID/GC trace of pyrolysis products from β *Pinus radiata* bark with major components identified.

The ash content of the char was 5.4% (Table 2). The differences in ash composition probably reflect differences in soil contamination arising from the felling and milling operations on the respective trees from which bark samples were obtained. One particular interest in carrying out this study was the possibility of producing electrolytic grade carbon from the char, for which use pyrolysis of beech was once studied (Thomas 1961). However, the high silica content of the ash makes it undesirable for the production of electrolytic grade carbon.

TABLE 2–Analysis of inorganic content of char product from pyrolysis of *Pinus radiata* bark from two sources (percentage of the char)

	Taupo	Kaingaroa
Silica	0.81	0.27
Calcium	0.95	0.42
Aluminium	1.80	0.19
Iron	0.46	0.03
Potassium	0.29	0.08
Chlorine	0.30	0.09
Titanium	0.08	0.03
Sulphur	0.12	0.04
Phosphorus	0.06	0.02
Magnesium	0.15	0.09
Sodium		0.06
Manganese		0.02

CONCLUSIONS

Significant yields of catechol and related compounds are available from pyrolysis of *P. radiata* bark. Since catechol is a higher-value phenol (~$5,000/tonne), pyrolysis may be of commercial interest. The yield of phenolics is dependent upon pyrolysis temperature. The presence of ethyl phenols and eugenol indicate that lignin is a component of *P. radiata* bark. Silica is a significant contaminant of the char from bark pyrolysis.

REFERENCES

ANON. 1989: Inexpensive phenol replacements move towards commercialisation. *SERI S & T In Review, Fall*: 12–13.

DONNOT, A.; RENINGOVOLO, J.; MAGNE, P.; DEGLISE, X. 1985: Flash pyrolysis of tar from the pyrolysis of pine bark. *Journal of Analytical and Applied Pyrolysis 8*: 401–14.

KUMAR, A.; MANN, R.S. 1982: Pyrolysis of poplar bark. *Journal of Analytical and Applied Pyrolysis 4*: 219–26.

LOMAX, T.D.; FRANICH R.A. 1990: Pyrolysis products of *Pinus contorta* bark. *New Zealand Journal of Forestry Science 20*: 349–52.

MARKHAM, K.R.; PORTER, L.J. 1973: Extractives of *Pinus radiata* bark. 1.Phenolic components. *New Zealand Journal of Science 16*: 751–61.

THOMAS, B.R. 1961: Wood charcoal as a source of electrode carbon. *DSIR, Dominion Laboratory Report No. 2048.*

UPRICHARD, J.M. 1991: Chemistry of wood and bark. Pp. 4-1–4-45 *in* Kininmonth, J.A.; Whitehouse, L.J. (Ed.) "Properties and Uses of New Zealand Radiata Pine" Vol.1. New Zealand Ministry of Forestry, Forest Research Institute, Rotorua.

van WYK, J.L. 1990: Wood residues: Who buys the byproduct? *New Zealand Forest Industries 21(6)*: 35–6.