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Analysis of biomass pyrolysis liquids: separation and characterization of phenols

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ABSTRACT

The liquid products derived from biomass (fir wood) pyrolysis were separated by silica gel open-column chromatography. A fraction rich in *ortho*- and non-*ortho*-substituted alkylarylphenols was isolated. This fraction was characterized by thin-layer chromatography and gas chromatography and was identified by IR, ^{1}H and ^{13}C NMR spectroscopy and was subjected to gas chromatographic–mass spectrometric analysis. About 12–17% (w/w) of the pyrolysis liquid products consisted of phenols, and the fraction rich in phenols contained phenol and other substituted phenols (85–95%, w/w). Aryl ethers can be produced by catalytic alkylation of the phenolic compounds.

INTRODUCTION

Phenols found in coal and biomass pyrolysis liquids are important compounds of increasing interest [1–5]. Phenols can be used as pure substances, as food antioxidants and gasoline additives or as precursors for the production of other chemicals, such as colorants, pesticides and aromatic ethers. Phenols are among the main constituents of biomass pyrolysis liquids [6].

Several methods have been used for separating and obtaining phenol-rich fractions. The most important are liquid–liquid extraction [7], ion-exchange chromatography [8] and silica gel column chromatography [9]. For the chemical characterization and identification of the phenolic components, chromatographic techniques [thin-layer chromatography (TLC), gas chromatography with flame ionization detection (GC–FID), high-performance liquid chromatography (HPLC)] [10–13] and spectroscopic methods (IR, ^{1}H and ^{13}C NMR, Fourier transform IR) have been applied [6,14,15]. Also analysis with gas chromatography–mass spectrometers (GC–MS) have also proved very versatile for this purpose [16,17].

In this work, a modified method was applied for separating the phenolic fraction from biomass pyrolysis liquids by silica gel open-column chromatography. Owing to the small amounts of pyrolytic liquids obtained, a phenol-rich fraction was isolated and not individual phenols. Alkaline extraction of the phenol-rich fraction was applied. Analysis and characterization of the phenolic fraction obtained were performed by TLC, GC–FID, IR, ^{1}H and ^{13}C NMR spectroscopy and GC–MS. For the first time, the phenolic compound 2,6-bis(1,1-dimethylethyl)-4-methylphenol was identified among the alkylphenols present in fir wood pyrolysis phenolic liquids.

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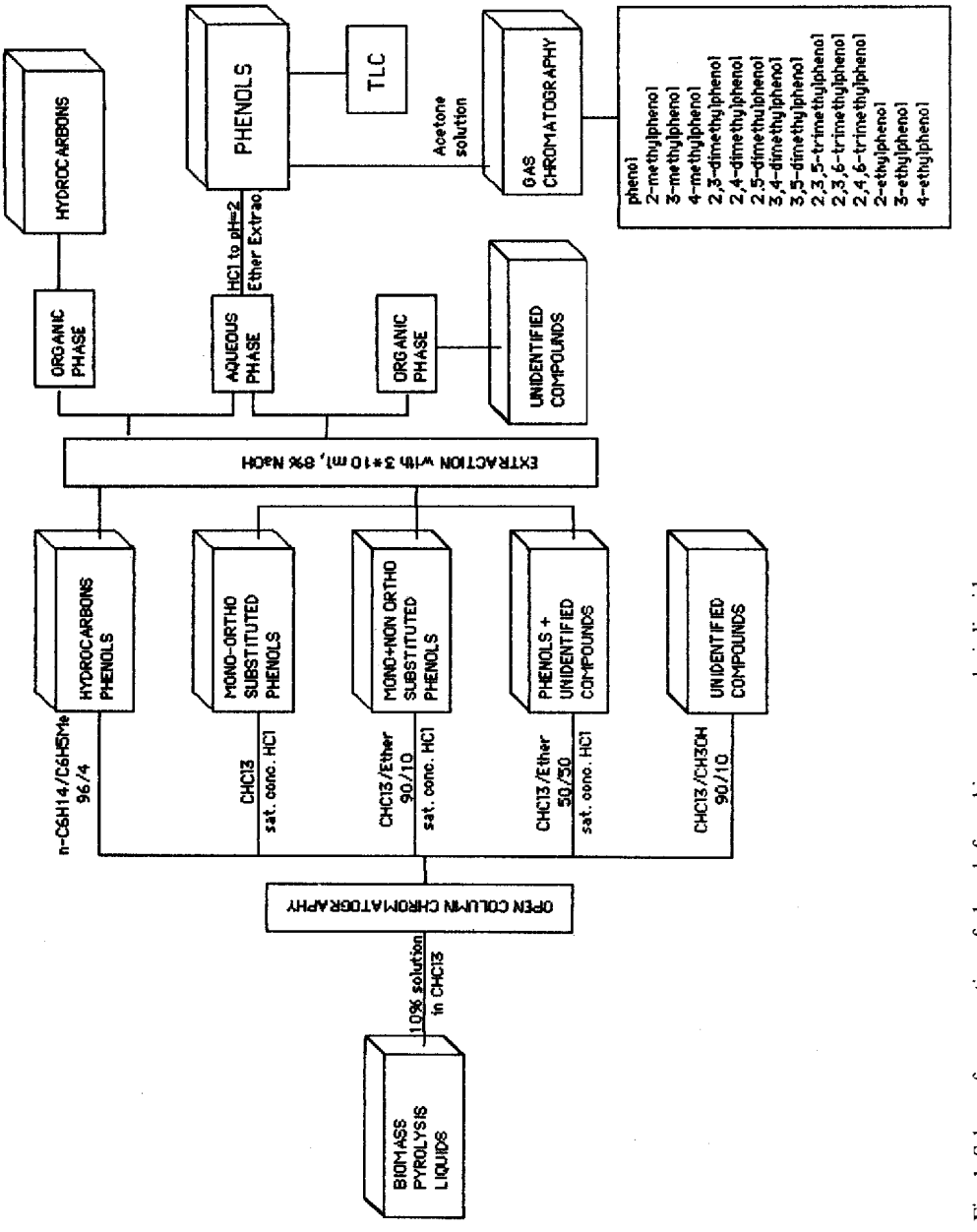

Fig. 1. Scheme for separation of phenols from biomass pyrolysis liquids.

EXPERIMENTAL

Materials

All solvents used were Merck LiChrosolv products. The biomass pyrolysis liquids were obtained by the reported procedure [18]. Phenol standards were obtained commercially (Merck, Supelco) and were used without further purification.

Silica gel open-column chromatography

A slurry column packed with 20 g of silica gel (70–140 mesh) in *n*-hexane–toluene (96:4) was prepared according to the method described by Schabron *et al.* [9]. This was carried out under a nitrogen atmosphere, with a silica-to-biomass pyrolysis liquids ratio of 20:0.1 [18]. As shown in Fig. 1 a procedure involving successive elutions with solvents of increasing polarity was followed. The first fraction was extracted with 10 ml of 8% sodium hydroxide solution. After phase separation and solvent removal, a yellow residue remained, which was weighed to an accuracy of 0.0001 g and was defined as "hydrocarbons". This residue was not characterized. The other three fractions were combined and extracted three times with 10 ml of 8% sodium hydroxide solution. This procedure was followed by acidification with concentrated hydrochloric acid. Extraction with diethyl ether gave a brown liquid rich in phenols, which was weighed and defined as the "phenolic fraction". This technique was first tested with model mixtures that contained representative phenolic components. The recovery of phenols was over 95% [19].

Instrumentation

A LECO CHN-800 microanalyser was used for elemental analysis of the phenolic fraction.

^{1}H NMR spectra were recorded on a Varian T-60 NMR spectrometer in deuterochloroform ($C^{2}HCl_3$)–tetramethylsilane (TMS) as internal standard, and ^{13}C NMR spectra were obtained on a Bruker WP-80 NMR spectrometer in $C^{2}HCl_3$–TMS.

The phenolic fraction was spot tested on plastic TLC sheets with silica gel 60 F_{254} and observed under long-wavelength ultraviolet light [10]. In addition, TLC was applied to the product of the characteristic reaction of diazotized *p*-nitroaniline with phenols, performed according to Crump's method [11]. The same method was applied using pure alkylphenols.

IR spectra of the biomass pyrolysis liquid samples were recorded on a Beckman IR 18-A spectrophotometer in $C^{2}HCl_3$ and tetrahydrofuran (THF). IR spectra (KBr) of the phenolic fraction were measured on a Model 1430 ratio recording IR spectrometer.

GC of the pyrolysis liquids was carried out on a Hewlett-Packard Model 5710A gas chromatograph equipped with a flame ionization detector and an Autolab computing integrator. A stainless-steel 6 ft. × $\frac{1}{8}$ in. I.D. column was used with 0.1% SP-1000 on 80–100-mesh Carbopack C. The carrier gas was helium at a flow-rate of 20 ml/min. The temperature programme was 170°C for 16 min, increased to 220°C at 2°C/min and maintained at that temperature for the remainder of the run.

GC–MS was performed on a QMD 1000 GC–MS system (Carlo Erba) equipped with a J&W DB-WAX fused-silica capillary column (60 m × 0.32 mm I.D.)

with a film thickness of 0.5 μm. The temperature was programmed as follows: 66°C for 1 min, 66–200°C at 20°C/min, for 10 min and 200–300°C at 10°C/min. For MS the scan rate was 1 s per scan with electron impact ionization at 70 eV, 200 μA. GC–MS as also performed on an ITD system (Finnigan MAT), equipped with a 25-m SE-54 capillary column directly coupled to the ITD.

RESULTS AND DISCUSSION

Analysis of the biomass pyrolysis liquids

Table I lists the average composition of typical biomass (fir wood) liquids [20], obtained from pyrolysis reactors described recently [18].

The IR spectra of the soluble portion from the biomass pyrolysis liquids, C^2HCl_3 (3380–3880 cm^{-1}) and THF (1500–1800 cm^{-1}), revealed strong absorptions. At 3690 cm^{-1} water absorption was observed, whereas at 3600 cm^{-1} free phenolic OH was indicated. Also, the peak at 3470 cm^{-1} showed the presence of pyrrolic NH. Three carbonyl bands were observed in THF solutions, similar to those reported by Dooley *et al.* [14]. These carbonyl bands are believed to show the presence of carboxylic acids (1735 cm^{-1}), associated acids or ketones (1700 cm^{-1}) and aromatic amides (1680 cm^{-1}).

The ^1H NMR spectra contained two major regions of signals around δ 1–5 ppm and δ 6–9 ppm, due to aromatic and aliphatic protons, indicating concentrations of methoxyl or other alkyl and aryl ethers. The same region of signals was observed by Boocock *et al.* [7] in oil fractions derived from hydrogenation of aspen wood.

Analysis of the phenolic fraction

Elemental analysis of the phenolic fraction gave the results shown in Table II. The oxygen content appeared to be very high, possibly owing to phenols and other oxygen-containing compounds (keto acids, esters, alkyl aryl ethers, etc.).

TLC gave for this fraction 4–7 populations that can be observed under long-wavelength UV light and can be detected with a spray reagent, *e.g.*, Folin's reagent.

Reaction of the phenolic fraction with diazotized 4-nitroaniline according to the method proposed by Crump [11] produced a mixture of 2- and 3-coupled stable dyes of yellow-orange colour. This reaction forms the basis of many well known quantitative methods for the determination of phenols.

The mobile phase used was benzene–cyclohexane–dipropylene glycol (30:70:3, v/v/v) and the papers were impregnated with formamide (Fig. 2). TLC single spots

TABLE I

AVERAGE COMPOSITION OF PYROLYSIS LIQUIDS

Compound	Concentration (%, w/w)
Hydrocarbons	14 ± 3
Phenols	15 ± 2
Unidentified (by difference)	71 ± 6

TABLE II

ELEMENTAL ANALYSIS OF THE PHENOLIC FRACTION

Element	Concentration (%, w/w)
C	72.3
H	8.3
O	18.8
N	0.6

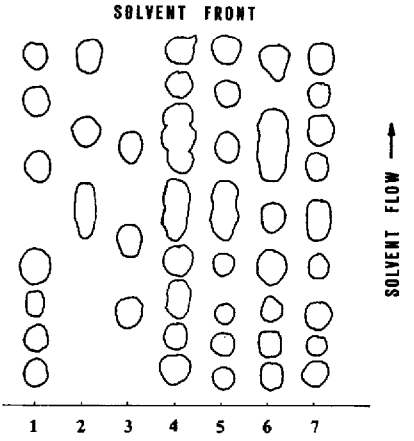

Fig. 2. Thin-layer chromatography. 1 = Mixture of phenol and methyl- and ethylphenols; 2 = mixture of dimethylphenols; 3 = mixture of trimethylphenols; 4 = mixture of pure phenols; 5 = sample A; 6 = sample B; 7 = sample C.

TABLE III

TLC R_F VALUES AND IDENTIFICATION OF PURE ALKYLPHENOLS (SINGLE SPOTS)

Phenol	2-Nitrophenylazo dyes			3-Nitrophenylazo dyes		
	R_F	Colour		R_F	Colour	
		Before ammonia treatment	After ammonia treatment		Before ammonia treatment	After ammonia treatment
Phenol	0.15	Orange-yellow	Yellow	0.14	Yellow	Rose
2-Methylphenol	0.35	Orange-yellow	Rose	0.34	Yellow	Mauve
3-Methylphenol	0.30	Orange-yellow	Orange	0.28	Yellow	Magenta
4-Methylphenol	0.98	Orange-yellow	Red	0.99	Orange	Purple
2-Ethylphenol	0.61	Orange-yellow	Orange	0.57	Yellow	Mauve
3-Ethylphenol	0.50	Orange-yellow	Yellow	0.48	Yellow	Magenta
4-Ethylphenol	1.00	Orange-yellow	Red	1.00	Orange	Purple
2,3-Dimethylphenol	0.57	Orange-yellow	Rose	0.47	Yellow	Lilac
2,5-Dimethylphenol	0.64	Orange-yellow	Red	0.50	Yellow	Lilac
2,6-Dimethylphenol	0.90	Orange-yellow	Rose	0.74	Yellow	Lilac
3,5-Dimethylphenol	0.46	Orange-yellow	Orange	0.42	Yellow	Brown
2,3,6-Trimephenol	0.60	Orange-yellow	Red	0.61	Yellow	Red
2,4,6-Trimephenol	0.36	Orange-yellow	Orange	0.38	Yellow	Mauve
2,3,5-Trimephenol	0.85	Orange-yellow	Rose	0.84	Orange	Purple

TABLE IV

MAIN BANDS OF THE IR SPECTRA OF THE PHENOLIC FRACTION

Wavenumber (cm^{-1})	Origin
3600–3200	O–H stretching vibration
2920–2940	C–H substituted on aromatic ring stretching vibration
1710	Carbonyl stretching, unconjugated
1595–1497	Common benzene skeletal vibration
1359	O–H bending vibration
1220	Characteristic C–OH stretching vibration of phenolics

following ammonia treatment gave a variety of colours including purple, rose, lilac and red-brown due to the reaction of 2- and 3-nitrophenylazo dyes with ammonia (Table III).

The main bands of the IR spectra of the phenolic fraction are given in Table IV.

Integration of the peaks in the ^{13}C NMR (δ, C^2HCl_3–TMS) spectra showed carbons attached to the phenolic hydroxyls. On the basis of these observations, the carbons appearing in the region δ 150–155 ppm indicate the presence of monophenols, whereas those in the region δ 140–146 ppm show the presence of heavy phenols. These observations are in good agreement with the literature [7].

In addition to the qualitative spectroscopic techniques applied to the phenolic fraction, GC analysis was also carried out using anisole and eugenol as internal standards. Identification and determination of phenolic components was based on matching relative response factors (RRF) of pure phenol standards. The results shown in Table V correspond to the phenolic fraction, the phenol separation of which appears in Fig. 3. There are some unidentified peaks because it was not possible to

TABLE V

CHEMICAL COMPOSITION OF THE PHENOLIC FRACTION DERIVED FROM GC ANALYSIS

Compound	Absolute amount (g)	RRF	Weight% (av.)
Phenol	0.00561	0.3637	3.4657
2-Methylphenol	0.00228	2.3800	1.4096
3-Methylphenol	0.00199	0.5163	1.2271
4-Methylphenol	0.00193	0.4836	1.1925
2-Ethylphenol	0.00005	0.5469	0.0291
3-Ethylphenol	0.00020	0.6272	0.1217
4-Ethylphenol	0.00013	0.6634	0.0810
2,6-Dimethylphenol	0.00017	0.5141	0.1037
2,4- and 2,5-Dimethylphenol	0.00117	0.5371	0.7231
2,3- and 3,5-Dimethylphenol	0.00076	0.6075	0.4679
3,4-Dimethylphenol	0.00028	0.6796	0.1736
2,4,6-Trimethylphenol	0.00023	0.5872	0.1426
2,3,6-Trimethylphenol	0.00022	0.6138	0.1377
2,3,5-Trimethylphenol	0.00025	0.7857	0.1512

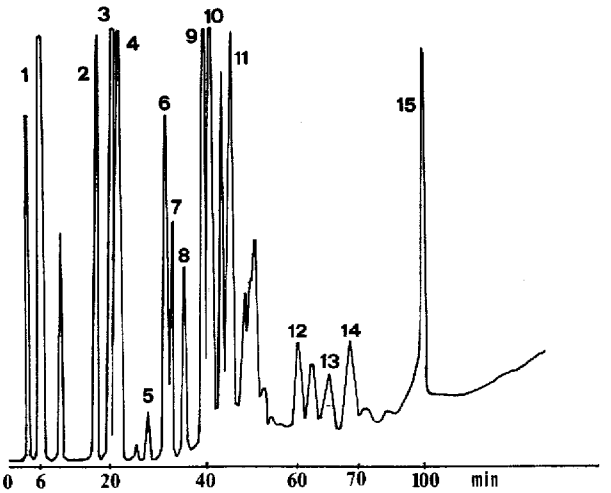

Fig. 3. Phenol separation on 6 ft. × 1/8 in. I.D. stainless-steel GC column of 0.1% SP-1000 on Carbopack C. Carrier gas, helium at a flow-rate of 20 ml/min. Temperature programme: 170°C for 16 min, 170–220°C at 2°C/min. Peaks: 1 = phenol; 2 = 2-methylphenol; 3 = 3-methylphenol; 4 = 4-methylphenol; 5 = 2-ethylphenol; 6 = 3-ethylphenol; 7 = 4-ethylphenol; 8 = 2,6-dimethylphenol; 9 = 2,4- and 2,5-dimethylphenol; 10 = 2,3- and 3,5-dimethylphenol; 11 = 3,4-dimethylphenol; 12 = 2,4,6-trimethylphenol; 13 = 2,3,6-trimethylphenol; 14 = 2,3,5-trimethylphenol; 15 = eugenol (internal standard).

find other commercially available phenol standards. The total proportion of light alkylphenols listed in Table V was calculated to be 9% (w/w) of the phenolic fraction [21].

The impossibility of finding more phenol standards for GC led to more sophisticated methods of analysis. Samples of phenolic fractions were also subjected to GC–MS. Figs. 4 and 5 show the total ion currents (TIC) for the same selected sample.

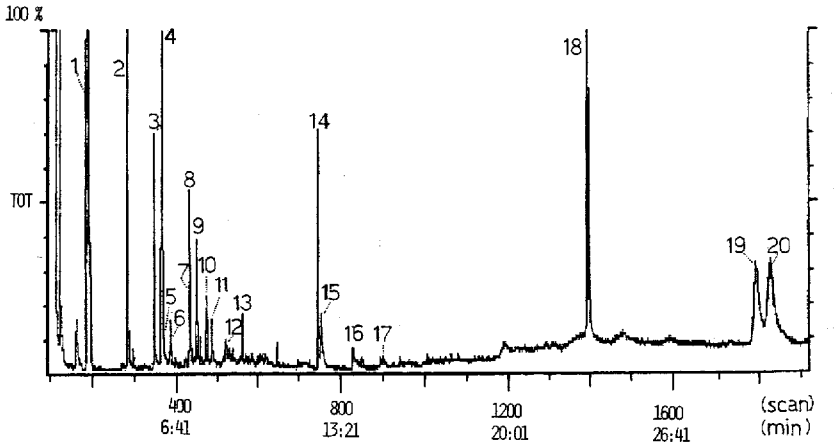

Fig. 4. Total ion current GC–MS (Carlo Erba) of the phenolic fraction of biomass pyrolysis liquids. For peak identification see Table VI.

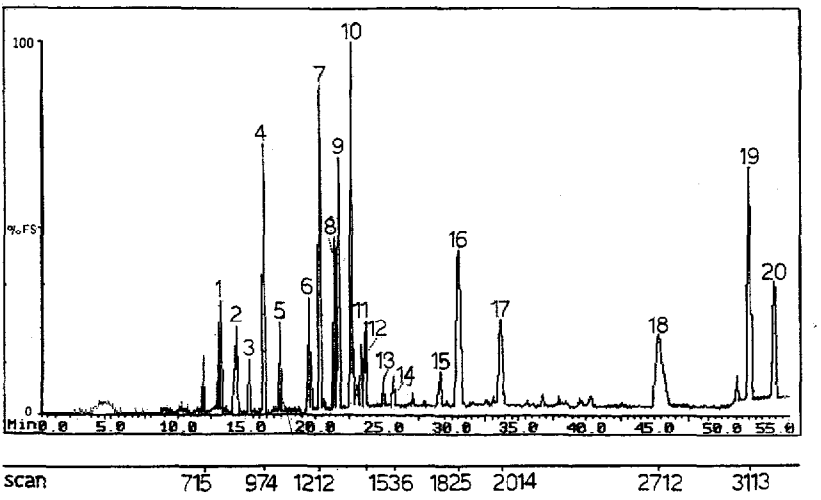

Fig. 5. Total ion current GC–MS (Finnigan Mat) of the phenolic fraction of biomass pyrolysis liquids. For peak identification see Table VII.

TABLE VI

COMPOUNDS IDENTIFIED BY GC–MS OF PHENOLIC FRACTION OF BIOMASS PYROLYSIS LIQUIDS (CARLO ERBA INSTRUMENT)

Peak No.[a]	Scan	Compound	*m/z*	Formula	Fragment ions[b]	Confirmation by comparison with standards[c]
1	187	2,3-Dimethyl-2-pentanol	78	C_7H_6O	59,101,83	×
2	282	Phenol	94	C_6H_6O	94,66,65	×
3	345	2-Methylphenol	108	C_7H_8O	108,107,79	×
4	362	4-Methylphenol	108	C_7H_8O	107,108,79	×
5	385	2,4-Dimethylphenol	122	$C_8H_{10}O$	107,122,121	×
6	390	3-Methylphenol	108	C_7H_8O	107,108,77	×
7	429	2,3-Dimethylphenol	122	$C_8H_{10}O$	107,122,121	×
8	446	2-Ethylphenol	122	$C_8H_{10}O$	107,122,77	×
9	455	3,5-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
10	482	Ethenyloxybenzene	120	C_8H_8O	91,120,65	×
11	487	1-Octanol	130	$C_8H_{18}O$	41,56,43	×
12	546	2,6-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
13	573	Methyl octanoate	158	$C_9H_{18}O$	74,87,43	×
14	741	2,6-Bis(1,1-dimethylethyl)-4-methylphenol	220	$C_{15}H_{24}O$	205,115,57	×
15	750	2-Naphthol	144	$C_{10}H_8O$	115,144,117	
16	823	2-Methyl-1-naphthol	158	$C_{11}H_{10}O$	158,129,115	
17	887	(1,1-Biphenyl)-3-ol	170	$C_{12}H_{10}O_2$	170,141,115	×
18	1400	2,3,6-Trimethylphenol	136	$C_9H_{12}O$	45,121,136	×
19	1780	3-(2-Hydroxyphenyl)-2-propenoic acid	164	$C_9H_8O_3$	120,91,65	
20	1840	1-(2-Hydroxyphenyl)ethanone	148	$C_8H_8O_2$	121,136,93	

[a] Peak numbers refer to the chromatogram in Fig. 4.

[b] The three most intense fragment ions from each 70-eV electron impact (EI) mass spectrum are given in order of decreasing intensity.

[c] Intensities were confirmed by comparing the retention indices and EI fragmentation patterns with those of standard compounds. Agreement between retention indices of the standard and sample species was typically within 1 unit.

Peak identification was performed partly by GC–MS and partly by the use of appropriate GC standards (Tables VI and VII). Twenty compounds were identified in the phenolic fraction. Good agreement of the two separate GC–MS analyses was observed (Tables VI and VII). It is important to mention here that 2,3-bis(1,1-dimethylethyl)-4-methylphenol was identified in both GC–MS analyses.

Of these twenty compounds the characteristic mass spectra of two representative phenols are considered here. The computer library matches of the mass spectra in many instances appeared fairly good (Figs. 6b, 7b and 8b). Fig. 6a displays the mass spectra of an unknown compound of the phenolic fraction. The fragment of *m/z* 94 is very stable and characteristic of the phenol parent ion $[M]^+$. In addition, the fragments of *m/z* 66, 65 and 39 derived from $[M-CO]^+$, $[M-CHO]^+$ and $[M-C_3H_3]^+$ are also characteristic ion fragments of this phenol. The computer library search (Fig. 6b) shows that phenol was the unknown compound. Phenol was also identified by TLC (Fig. 2) and GC (Fig. 3).

Similarly, in Figs. 7 and 8, the fragments of *m/z* 205, 220, 177, 119 and 57 indicate the presence of 2,6-bis(1,1-dimethylethyl)-4-methylphenol. In addition to the

TABLE VII

COMPOUNDS IDENTIFIED BY GC–MS ANALYSIS OF A PHENOLIC FRACTION OF BIOMASS PYROLYSIS LIQUIDS (FINNIGAN MAT INSTRUMENT)

Peak No.[a]	Scan	Compound	*m/z*	Formula	Fragment ions[b]	Confirmation by comparison with standards[c]
1	870	Phenol	94	C_6H_6O	94,66,65	×
2	885	2-Methylphenol	108	C_7H_8O	108,107,79	×
3	974	4-Methylphenol	108	C_7H_8O	108,107,79	×
4	1100	3-Methylphenol	108	C_7H_8O	108,107,79	×
5	1180	2-Ethylphenol	122	$C_8H_{10}O$	107,122,77	×
6	1212	2,4-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
7	1250	2,3-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
8	1311	3,5-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
9	1358	2,6-Dimethylphenol	122	$C_8H_{10}O$	107,122,77	×
10	1420	1-Octanol	130	$C_8H_{18}O$	41,56,43	×
11	1465	Methyl octanoate	158	$C_9H_{18}O$	74,87,43	×
12	1484	2-Naphthol	144	$C_{10}H_8O$	115,144,177	×
13	1536	2-Methyl-1-naphthol	158	$C_{11}H_{10}O$	158,129,115	×
14	1770	2,6-Bis(1,1-dimethylethyl)-4-methylphenol	220	$C_{15}H_{24}O$	205,115,57	×
15	1800	2,3,6-Trimethylphenol	136	$C_9H_{12}O$	45,121,136	×
16	1826	(1,1-biphenyl)-3-ol	170	$C_{12}H_{10}O_2$	170,141,115	
17	2014	2,4,6-Trimethylphenol	136	$C_9H_{12}O$	45,121,136	
18	2712	1-(2-Hydroxyphenyl)ethanone	148	$C_8H_8O_2$	121,136,93	
19	3113	3-(2-Hydroxyphenyl)-2-propenoic acid	164	$C_9H_8O_3$	121,136,93	
20	3180	1-(3-Hydroxyphenyl)ethanone	148	$C_8H_8O_2$	121,136,93	

[a] Peak numbers refer to the chromatogram in Fig. 5.

[b] The three most intense fragment ions are given in order of decreasing intensity.

[c] Intensities were confirmed by comparing the retention indices and EI fragmentation patterns with those of standard compounds. Agreement between retention indices of the standard and the phenolic sample was the same as with the Carlo Erba instrument.

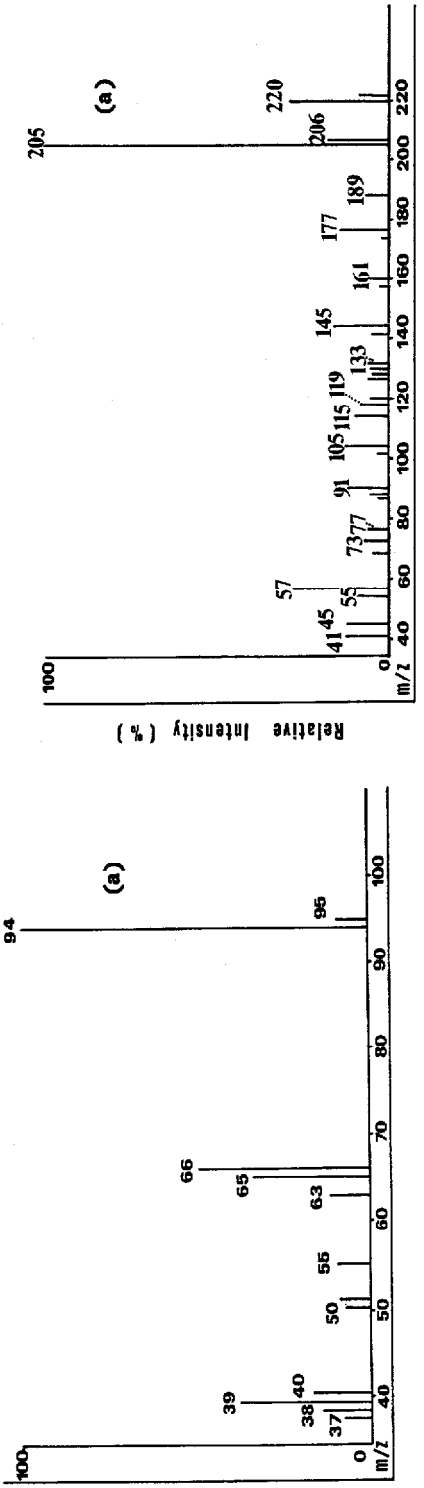

Fig. 6. (a) Mass spectrum of unknown compound in scan 282 and (b) its computer library search.

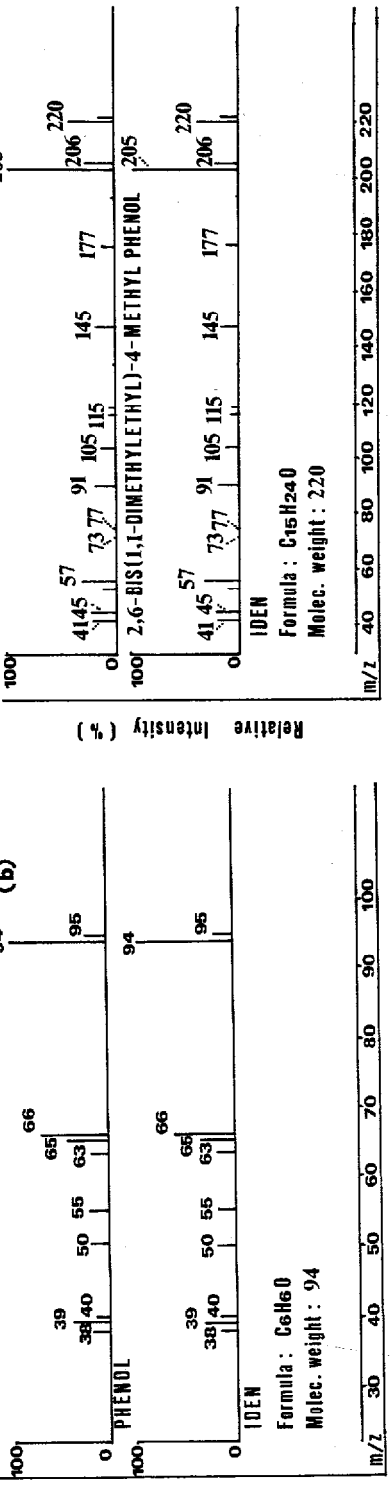

Fig. 7. (a) Mass spectrum of unknown compound in scan 741 and (b) its computer library search.

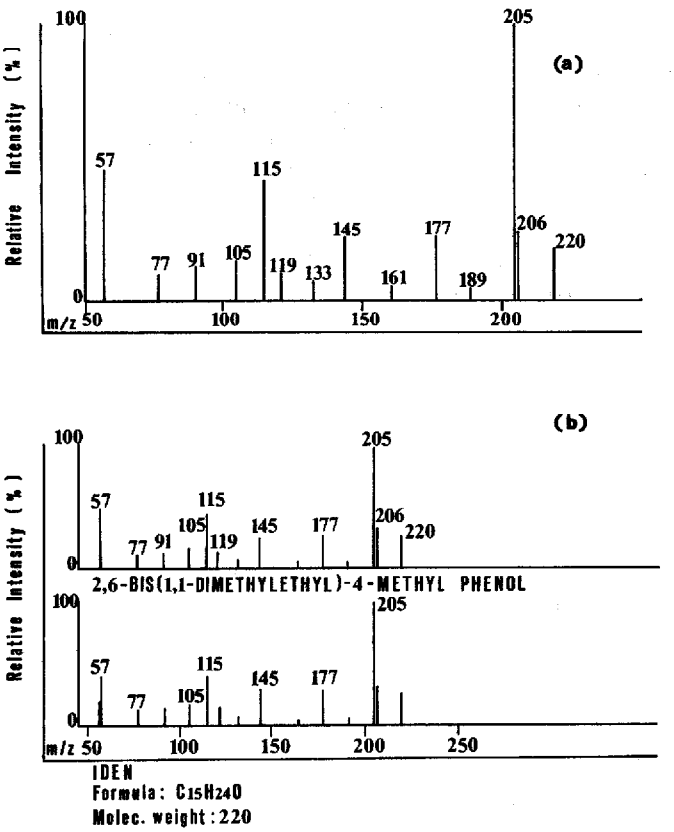

Fig. 8. (a) Mass spectrum of unknown compound in scan 1770 and (b) its computer library search.

two separate computer library searches of the phenolic fraction, the mass spectrum of the pure phenol in question was measured. It appeared that the pure phenol gave exactly the same fragments as those shown in the GC–MS analyses of the phenolic sample. It is important to mention that the aforementioned phenol was identified for the first time in fir wood pyrolysis liquids. In the same way, other phenolic compounds characterized and found to be present in decreasing abundance were 2-, 3- and 4-methylphenols, ethenylphenol, ethenyloxybenzene, dimethylphenols, 2-naphthol, 1-(2-hydroxyphenyl)ethanone, (1,1-biphenyl)-3-ol, 3-(2-hydroxyphenyl)-2-propenoic acid and 2,3,6- and 2,4,6-trimethylphenols. The methylphenols, dimethylphenols, ethylphenols and trimethylphenols were also identified by TLC and GC (Figs. 2 and 3). These compounds have also been reported by other workers [1–5].

Lack of high-field NMR equipment restricted our analysis to the techniques mentioned above. However, high-field NMR analysis is desirable in future work.

It was estimated qualitatively that non-*ortho*- and *ortho*-substituted alkylphenols comprise 70% and 30% of the phenolic fraction, respectively. The amount of non-removable solvents, from the pyrolysis liquids and from the phenolic fraction in the different separation techniques was about 4% as determined by GC.

CONCLUSIONS

The recovery of phenols using acidified silica gel column chromatography was over 95% (w/w). Good separation and characterization of the phenolic fraction was achieved after combining open-column chromatography with alkaline extraction.

The phenol content in biomass pyrolysis liquids was found to be 12–17% (w/w). The phenolic fraction of biomass pyrolysis liquids consisted mainly (85–95%, w/w) of light and heavy non-*ortho*- and *ortho*-substituted alkylphenols, with a non-*ortho*-to-*ortho* ratio of 2:3. The light alkylphenol content was calculated to be about 9% (w/w) of the phenolic fraction. 2,6-Bis(1,1-dimethylethyl)-4-methylphenol was identified in the phenolic fraction.

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