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Analysis of biomass pyrolysis oils by a combination of various liquid chromatographic techniques and gas chromatography–mass spectrometry

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ABSTRACT

A strategy for the overall analysis of pyrolysis oils is decribed based on the combination of a previously developed fractionation, the improved API 60 fractionation, with high-performance analytical techniques used in series, such as size-exclusion chromatography and capillary gas chromatography–mass spectrometry. As an example, the results obtained for the neutral and acid fractions resulting from the improved API 60 fractionation of pyrolysis oils prepared by carbonization of different species (hornbeam, poplar, pine) are given.

INTRODUCTION

Successive world energy crises and large increases in the prices of oil derivatives have caused renewed interest in the different possibilities offered by the valorization of biomass as an energy source and in the chemical exploitation of wood pyrolysis by-products.

Pyrolysis oils can be considered as a real source of useful chemicals. Although product such as acetic acid or methanol are now more easily obtained from synthetic processes, the situation is different for numerous chemicals extractable from pyrolysis oils. Unfortunately, pyrolysis oils, which are very complex matrices constituted by hundreds of compounds with very different polarities, change with time. This instability is unquestionably a handicap in their exploitation and consequently their valorization. The stabilization of pyrolysis oils requires first the chemical and structural characterization of this complex matrix. Unlike pyroligneous acids, which are well known and have been the subject of many studies [1–5], few structural data are available on tars from biomass. Until recently studies on these organic matrices were

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mainly oriented towards the identification of particular compounds families, *e.g.*, polycyclicaromatic hydrocarbons [6–9], phenols [9–14], light fatty acids [15–18] and carbonyl compounds [19,20].

In 1986 Elliott [21,22], using capillary gas chromatography (GC) and mass spectrometry (MS), characterized for the first time the tars resulting from wood carbonization. This fundamental study constitutes the first overall approach to the analysis of wood carbonization tars as previously only a detailed identification of polyaromatic hydrocarbons had been reported [23]. However, the method used by Elliott to simplify the organic matrix prior to analysis by GC—MS, *viz.*, extraction with dichloromethane, was limited because of the low solubility of highly polar compounds in this solvent. Consequently, the results obtained, although very interesting, give an overestimation of low-polarity compounds to the detriment of high-polarity compounds. In order to avoid these difficulties, we decided to use a set of liquid chromatographic techniques to fractionate the complex organic matrix of pyrolysis oils. We adapted several techniques developed for the analysis of heavy oil residues [24,25], *i.e.*, the coupling of chromatographic and spectroscopic techniques, to obtain information about the structure of pyrolysis oils.

EXPERIMENTAL

Reagents

Cyclohexane, benzene, methanol, acetonitrile and tetrahydrofuran (THF) used for preparative ion-exchange chromatography were obtained from Merck (Darmstadt, Germany) and were purified by distillation. Water was purified by reverse osmosis and filtration using a Milli-RO + Milli-Q system from Millipore (Molsheim, France).

The water content of oils was determined using a Karl Fischer Automat E 547 apparatus (Metrohm, Herisau, Switzerland) with the reagents Re Aquant titrant and Re Aquant solvent (Baker, Deventer, The Netherlands).

Preparative ion-exchange chromatography

Ion-exchange chromatographic fractionations were performed using a preparative system built in our laboratory as described previously [26]. The experimental assembly was a modular component system consisting of a Model MCP 110 pneumatic pump (Haskel, Burbank, CA, U.S.A.), a pulse damper (Touzart et Matignon, Vitry/Seine, France), a splitter (Waters Assoc., Milford, MA, U.S.A.) an injection valve (Rheodyne, Cotati, CA, U.S.A.) equipped with a 10-ml sample loop, a heat exchanger made from a 2.5 m × 1.65 mm I.D. length of stainless-steel tubing shaped in a spiral and fitted in a heating jacket and three three-way valves (Hoke, Cresskill, NJ, U.S.A.) allowing the columns either to be set on-line or to be by-passed. The different parts were connected with 4.7 mm I.D. stainless-steel tubing (Touzart et Matignon), except for the splitter–detector connection, where 0.25 mm I.D. stainless-steel tubing was used. The two columns utilized were two 30 cm × 2 cm I.D. sections of stainless-steel tubing one dry packed with 15–60-mesh Amberlite IRA 904 and the other with 16–50-mesh Amberlyst A15 (Rohm and Haas, Philadelphia, PA, U.S.A.).

In order to exhibit maximum effectiveness for pyrolysis oil applications, the resins must be converted to the hydroxide form (IRA 904) and hydrogen form (A15)

TABLE I

PREPARATION OF AND CONDITIONING PROCEDURE FOR ION-EXCHANGE RESINS

Resin	Washing	Neutralization	Activation	Neutralization	Conditioning for 8 h: solvent
A 15	CH_3OH–KOH (90:10)	Distilled water	CH_3OH–HCl (90:10)	Distilled water	CH_3OH, CH_3CN, benzene, cyclohexane
IRA 904	CH_3OH–HCl (90:10)	Distilled water	CH_3OH–KOH (90:10)	Distilled water	CH_3OH, THF, benzene, cyclohexane

according to a method derived from that recommended by Jewell [27] (Table I). Column I was packed with the anion-exchange resin and column II with the cation-exchange resin. Through control by two valves the circulating fluid was pumped through either one or both columns.

The sample (3.1 g) was dissolved using ultrasonic dispersion in the minimum volume of benzene–cyclohexane (75:25) and the solution was then fed into the sample loop injector. It must be noted that with fast pyrolysis oil, 17% of the sample is insoluble in this mixture, in contrast to the other samples, which are completely soluble. The elution sequence and the acid–base characteristics of the fractions collected are reported in Table II.

Size-exclusion chromatography

The apparatus consisted of a Model 6000 A dual-piston pump, a U6K universal injector, a model M 440 UV–visible detector and a R 401 differential refractometric detector (all from Waters Assoc.). The signals from the detectors were displayed on a Kipp & Zonen (Delft, The Netherlands) recorder.

The chromatographic separations were performed on two columns, a 5-μm μSpherogel 50 Å (300 mm × 7.7 mm I.D.) (Beckman, Fullerton, CA, U.S.A.) coupled with a 7-μm μStyragel 100 Å (300 mm × 7.7 mm I.D.) (Waters Assoc.). The flow-rate of the mobile phase (THF) was 0.6 ml/min.

GC analyses and GC–MS coupling

GC analyses were performed using a Hewlett-Packard Model 5880 A gas chromatograph fitted with a 25-m fused-silica column coated with CP Sil 5 (Chrompack, Middelburg, The Netherlands) and a flame ionization detector. The conditions used were as follows: carrier gas, nitrogen U (Air Liquide, St-Quentin en Yvelines, France), inlet pressure 0.9 bar; injector temperature, 275°C; detector temperature, 280°C; splitting ratio, 1:30; injection volume, 1 μl of a 10 mg/ml solution; temperature programme, isothermal at 40°C for 5 min, linear gradient at 3°C/min to 150°C, then at 4°C/min to 250°C, isothermal at 250°C for 30 min.

For GC–MS, a model R 10-10 quadrupole spectrometer (Delsi Nermag Instruments, Argenteuil, France) fitted with the same column as above was used. The chromatographic conditions were as follows: carrier gas, Helium U (Air Liquide), inlet pressure 0.7 bar; injector temperature, 240°C; interface temperature, 285°C; splitless injection, 10 s; injection volume, 2.5 μl of a 10 mg/ml solution. The mass spectrometric conditions analysis were as follows: repeller potential, 6.6 V; source potential, 6 V; filament current intensity, 180 mA; electron energy, 70 eV; mass range, 31–450 u.

Spectra were interpreted by matching the results with library spectra and with known fragmentation patterns obtained from standard compounds. These standard compounds are marked with asterisks in Tables IV–VI.

Samples

The pyroligneous oils were derived from the carbonization of different wood species (hornbeam, pine and poplar). The logs were dried in a drying stove at 105°C, then stored for 1 month under ambient conditions. The wood dryness was then 92–94%. The carbonization was performed at the Centre Technique Forestier Tropical, using a Herman-Moritz oven, using the following programme: for slow pyrolysis, linear temperature gradient from 20 to 110°C in 3 h, isothermal at 110°C for 18 h (drying), linear temperature gradient from 100 to 500°C in 5 h, isothermal at 500°C for 5 h (cooking), cooling for 20 h and for fast pyrolysis, linear temperature gradient from 20 to 500°C in 2 h, isothermal at 500°C for 1 h (cooking), cooling for 20 h.

The characteristics of the pyroligneous oils were as follows: hornbeam (slow pyrolysis), 49.3 g of oil from 100 g of dry wood, including 7.9 g of tar, specific gravity 1.18 g/ml; hornbeam (fast pyrolysis), 54.1 g of oil from 100 g of dry wood, including 8.5 g of tar, specific gravity 1.07 g/ml; pine (slow pyrolysis), 44.9 g of oil from 100 g of dry wood, including 10.5 g of tar, specific gravity 1.04 g/ml; poplar (slow pyrolysis), 36.8 g of oil from 100 g of dry wood, including 6 g of tar, specific gravity 1.07 g/ml.

RESULTS AND DISCUSSION

The strategy developed combines two liquid-phase chromatographic techniques (ion-exchange and size-exclusion chromatography) with coupled GC–MS. The pyrolysis oils (after thorough azeotropic dehydration) were submitted first to a functional sorting according to a technique derived from the API 60 procedure [28]. This method uses the differences in interactions in an organic medium between a solute and ion-exchange resins (styrene–divinylbenzene copolymers, bonded to sulphonates and ammonium moieties in cation and anion exchangers respectively). As the mobile phase is organic, there is strictly no ion exchange but rather an association between functional groups in the sample molecules and functional groups of the resins constituting the stationary phase. This association is more or less strong depending on the acid–base characteristics of the sample components.

The sample is deposited on the resin surface by means of a solvent (the least polar possible) compatible with its solubility. Bonds of different strengths are formed and are then progressively destroyed as a function of their nature by thorough elution using mobile phases of increasing polarity. Hence the components are eluted according to their increasing acid–base characteristics.

Originally, this chromatographic technique was long and tedious. Some years ago, it was improved in our laboratory [26] by means of the device described under Experimental. We can perform a complete acid–base separation in 7 h compared with

TABLE II

ELUTION SEQUENCE AND ACID–BASE CHARACTERISTICS OF THE FRACTIONS COLLECTED IN PYROLYSIS OIL ANALYSIS

Ion exchanger	Eluent	Acid–base characteristic of the fraction collected
A15 + IRA 904 (coupled)	Benzene–cyclohexane (75:25)	Neutral
IRA 904	Benzene	Weak acids
	Benzene–acetonitrile	Medium acids
	Acetonitrile	Strong acids
	Methanol	Very strong acids
A15	Benzene	Weak bases
	Benzene–THF	Medium bases
	THF	Strong bases
	Methanol	Very strong bases

more than 8 days using the original method, obtaining nine fractions with different acid–base characteristics.

As the improved API 60 method was developed for the analysis of heavy oil fractions, an adaptation was necessary for application to pyrolysis oils. Some of the solvents used in the separation of heavy oil fractions, such as acetic acid and diethylamine, are not suitable for the analysis of wood pyrolysis oils. These solvents gave solvates which were too stable. The elution sequence used to analyse pyrolysis oils and the acid–base characteristics of the fractions collected are reported in Table II.

The acid–base balances obtained after analysis of various species are reported in Table III. Yields were calculated with respect to the mass of dry tar injected. The main features of the results are as follows. The partitioning of acid–base fractions depends on the nature of both the wood species and the process (fast or slow pyrolysis). With hornbeam and poplar a similar acid–base balance is obtained, but the results are different for pine (softwood) pyrolysis. However, although mass balances

TABLE III

ACID–BASE REPARTITION OF PYROLYSIS OILS AS A FUNCTION OF WOOD SPECIES (MASS BALANCE)

Wood species	Acid–base characteristic of fractions collected			
	Neutral (%)	Acidic (%)	Basic (%)	Total yield (%)[a]
Hornbeam[b]	37	33.5	28	98.5
Pine[b]	65	16.5	13.5	95
Poplar[b]	35	29	27	91
Hornbeam[c]	54	22	18.5	94.5

[a] Calculated with respect to the dry tar mass injected before dissolution.

[b] Slow pyrolysis.

[c] Fast pyrolysis.

of poplar and hornbeam are similar, their qualitative compositions are different, as shown by the capillary gas chromatograms of the various acid–base fractions of their pyrolysis oils (see Fig. 1). The structures of the compounds attributed to the main peaks are given. The attributions made done by comparison of the chromatograms of neutral and acidic fractions and of GC–MS analyses of their neutral and acidic subfractions obtained after size-exclusion chromatography. With the basic fraction, the subfractions obtained after size-exclusion chromatography were still too complex to allow GC–MS analyses and no attribution was attempted. Totally different balances were obtained with the same species (here hornbeam) as a function of pyrolysis conditions (slow or fast). Finally apart from the neutral fraction, which is the most abundant regardless of wood species, the medium-acid fraction and the medium-basic fraction are predominant in acids and bases.

After this first separation, the organic matrix is fairly simplified, but the complexity of the fractions collected remains too great and impedes identification of the components by GC–MS. Therefore we applied a second preparative chromatographic step to the acid–base fractions collected. This second step is based on size-exclusion chromatography.

Size-exclusion chromatography has been applied in the field of wood liquefaction [29–31]. For instance, Shen *et al.* [32] performed such a separation and four

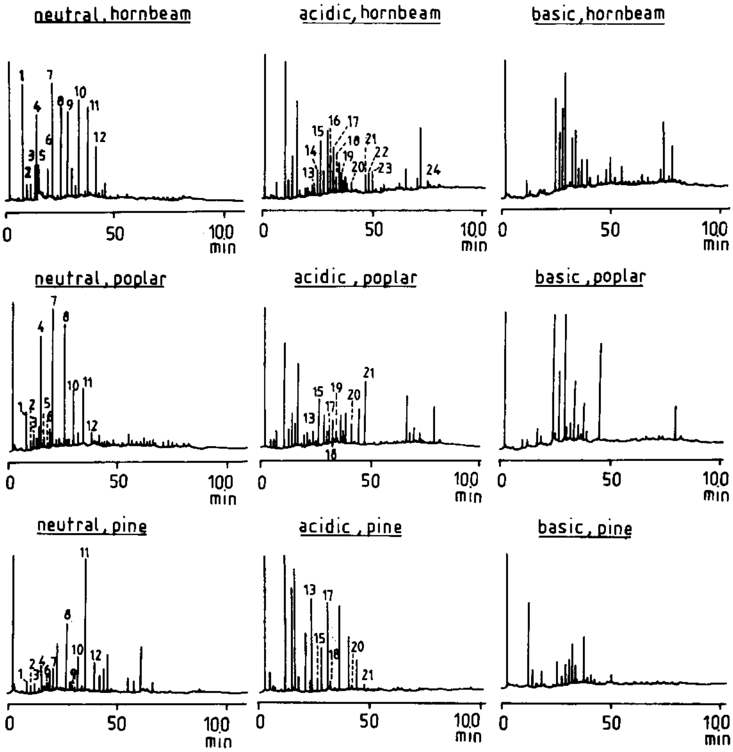

Fig. 1. Capillary gas chromatograms of various acid–base fractions of pyrolysis oils obtained by slow pyrolysis.

classes of components were separated from a pyrolysis oil: heavy hydrocarbons, light hydrocarbons and esters, phenolic derivatives and aromatic compounds.

We applied this technique of sorting as a function of molecular size of each of the fractions obtained from the API 60 separation. We resolved each of the acid–base fractions into three subfractions with different molecular weights. As an example, Fig. 2 shows the separations of the predominant acid–base fractions for hornbeam wood with slow pyrolysis. We checked that for all three subfractions obtained from each acid–base fraction, the recovery yields were quantitative within the experimental precision.

After this second preparative separation, we obtained 27 fractions for each of the pyrolysis oils analysed and we attempted to identify the components by capillary GC–MS. Every fraction was studied using two ionization modes: electron impact at 70 eV and chemical ionization by ammonia and methane. These two ionization modes are complementary: the former allows the fragmentation of molecules and gives important structural information and the latter is used to obtain molecular weights.

For each fraction, a comparision is made between the total ion current in the electron impact and chemical ionization modes. The molecular weight is then obtained for each peak on the gas chromatogram. After the determination of molecular weights, we searched for the ten best correlations between the electron impact mass spectra and the mass spectral library. Thus, we obtained the structures of a number of fragments and hypothetical structures were established. Among these hypothetical structures, the most likely according to the physico-chemical properties of the compound (acid–base characteristics, polarity and chromatographic behaviour) was retained.

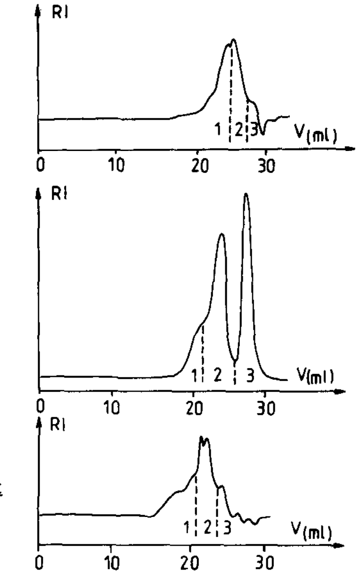

Fig. 2. Preparative high-performance size-exclusion chromatography of acid–base fractions from pyrolysis oils of hornbeam wood obtained by slow pyrolysis: (a) neutral fraction; (b) medium acid fraction: (c) medium basic fraction. *V* = Retention volume; RI = refractive index.

TABLE IV

CONSTITUENTS OF THE NEUTRAL FRACTION OF A HORNBEAM PYROLYSIS OIL OBTAINED BY SLOW PYROLYSIS

Compound[a]	Peak No.[b]
Esters, ketones and aldehydes	
Methylfuran carboxylate	
2-Butanone acetate	
Tetrahydrofuranyl acetate	
Propyl acetate	
Acetylcyclopentene	
Acetylcyclohexene	
Ethyl methylbenzoate	
Methyl dimethoxybenzoate	
Methyl hexadecanoate	
2-Pentanone*	
5-Methyltetrahydrofuranone	
Methylcyclopentanone	
Ethylmethylcyclopentanone	
(2-Methylfuryl)ethanone	
Indanone*	
(3-Ethylnaphthalene)-2-propanone	
Furfural*	
Methyltetrahydrofurfural	
Ethers	
Methyltetrahydrofuran	
Propyldioxolane	
Methoxytoluene	
2-Propylfuran	
Ethoxybenzene	
Dimethoxybenzene	
Ethylmethoxybenzene	
Dimethoxytoluene	4
Methylethyldihydropyran	
Ethylbutyldihydropyran	5
Dimethoxydimethylbenzene	
Dimethoxystyrene	
Diethoxybenzene	
Dimethoxyethylbenzene	
Dimethoxyethoxybenzene	7
Trimethoxybenzene	
Di-*tert.*-butylmethoxybenzene	8
Trimethoxybenzene	
Trimethoxyallylbenzene	
Dimethoxy methyldihydrobenzofuran	
(Methoxybenzofuryl)styrene	
Aromatics	
Isopropylbenzene*	
Indene*	
Propyltoluene	
Butylbenzene*	
Isopropyltoluene	
tert.-Butylbenzene*	
Aromatics	
Dimethylethyl benzene	
Diethyl benzene	1
Tetramethylbenzene	2
Ethylpropylbenzene	
3-Phenyl-1-butene	3
Methylindene	
Ethylstyrene	
Propylstyrene	
Pentylbenzene*	
Methylbenzofuran	
Naphthalene*	
Methyldibenzofuran	10
Dimethylbenzofuran	
Dibenzofuran	
Dimethylindane	
Methylnaphthalene	6
Methyltetrahydronaphthalene	
Ethyltetrahydronaphthalene	
Dimethylnaphthalene	
Propylnapthalene	
Propylallylnaphthalene	
Isopropylnaphthalene	
Isopropylbiphenyl	9
Dimethylbiphenyl	
Diethylbiphenyl	
Fluorene	
Methylfluorene	
Anthracene*	
Pyrene*	
Methylpyrene	
Acephenanthrylene	
Butylvinylnaphthalene	
Methylphenyl-2,3-dihydrobenzofuran	12
Benzofluorene	
Xanthene	
Methylisopropylnaphthalene	11
Hydrocarbons	
Ethylcyclopentene	
Propylcyclopentene	
Isopropylcyclopentene	
Isopropylcyclopentane	
2-Butylcyclopentane	
3-Methyl-4-octene	
Dimethylethylcyclohexadiene	
Tetramethylcyclohexadiene	
Dimethylundecane	
Tridecane*	
Tetradecane*	
Bicyclohexyl	
Dimethylbicyclohexyl	
Pentadecane*	
Hexadecane*	
Dipropyldodecane	
Methylheptadecane	

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[a] Asterisks indicate compounds identified by comparison with standards.

[b] Peak numbers are those of compounds labelled in Fig. 1.

The organic matrices obtained for the subfractions from size-exclusion chromatography of neutral and acidic fractions are so simple that the simplified procedure described above allowed us to attempt the identification of their likely structures. The structures identified in neutral fractions are reported in Table IV (classification by formulae). A similar classification of weak, medium, strong and very strong acidic fractions is reported in Tables V and VI.

TABLE V

CONSTITUENTS OF THE WEAK ACID FRACTION OF A HORNBEAM PYROLYSIS OIL OBTAINED BY SLOW PYROLYSIS

Compound[a]	Peak No.[b]	Compound[a]	Peak No.[b]
Phenols		*Lactone*	
Phenol*	13	Butyrolactone	
Methylphenol	14	*Esters, aldehydes and ketones*	
Dimethylphenol	16	Acetylfuran	
Ethylphenol		Acetoxymethylbenzofuran	
Methylethylphenol		Acetoxyethylbenzofuran	
Dimethoxyphenol		Methylfurfural	17
Propylphenol		Trimethylbenzaldehyde	
Isopropylphenol	20	Dimethylcyclohexanone	
Trimethylphenol	20	Methylheptanone	
Dimethylmethoxyphenol		*Ethers*	
Methylpropylphenol		Methoxypentane	
Diethylphenol		Dimethyl methoxybenzofuran	
Butenylphenol		Ethylmethoxybenzofuran	
Propenylmethoxyphenol		*Aromatic*	
Propenyldimethoxyphenol		Toluene*	
Trimethoxyphenol			
Propylmethoxyphenol			
Methyl methoxyhydroxybenzoate			
Dimethoxyhydroxybenzaldehyde			
Acetyldimethoxyphenol			
Propionyldimethoxymethylphenol			
Butyryldimethoxyphenol			

[a] Asterisks indicate compounds identified by comparison with standards.
[b] Peak numbers are those of compounds labelled in Fig. 1.

Some comments can be made on the basis of the results in Tables IV–VI. Micro-distillations of each of the fractions (neutral, acidic or basic) were performed at the temperature of the GC analysis. The proportion of compounds characterized under these conditions is estimated to be from 50 to 70%. The improved API 60 method appears to be an efficient technique for acid–base separation. The polarity of the components identified in each of the fractions increases when the acid–base characteristic become greater. Pyrolysis oils obtained after slow pyrolysis of wood contain mainly saturated hydrocarbons and aromatics (neutral fraction), ethers (peculiarly abundant in the neutral fraction), esters (in neutral and weak acid fractions), aldehydes and ketones (in the neutral fraction and weak, medium and strong acid fractions), phenols [containing monophenols (essentially in the weak and medium acid fractions) and naphthols and diphenols, only in the most polar fractions (medium,

TABLE VI

CONSTITUENTS OF THE MEDIUM, THE STRONG AND THE VERY STRONG ACID FRACTIONS OF A HORNBEAM PYROLYSIS OIL OBTAINED BY SLOW PYROLYSIS

Medium acids		Strong and very strong acids	
Compound	Peak No.[a]	Compound	Peak No.[a]
Organic acid		*Organic acids*	
Ethylbenzoic acid		2-Methylbutyric acid	
Naphthols and phenols (di- and mono-)		Methoxyhydroxybenzoic acid	
Ethylnaphthol		*Naphthols and phenols (di- and mono-)*	
Trimethylnaphthol		Dimethylnaphthol	
Ethylhydroxyphenol	19	Diethylnaphthol	
Dimethylhydroxyphenol		Methoxyacetylnaphthol	
Dihydroxyindane		Dihydroxybenzene	18
Methylhydroxy-1,2-dihydronaphthol		Methyldihydroxybenzene	
Methoxyphenol		Acetyldihydroxybenzene	
Allylethoxyphenol		Methylmethoxydihydroxybenzene	
Trimethylmethoxyphenol	22	Methylpropyldihydroxybenzene	
Allylethylphenol		Isopropyldihydroxybenzene	
Propylmethoxyphenol	21	Propyldihydroxybenzene	
Vinylmethoxyphenol		Isobutyldihydroxybenzene	
Allyformylphenol		Methylethyldihydroxybenzene	
Methyl methylhydroxybenzoate	23	Methoxypropyldihydroxybenzene	
Trimethylhydroxyindane		Methylpropionyldihydroxybenzene	
Methylhydroxyindane		Methyl dimethyldihydroxybenzoate	
Hexenylphenol		Methoxydihydroxybenzene	
Ethyldimethylbenzophenone		Methoxyphenol	15
Methyl dimethoxyhydroxybenzoate		Methyl hydroxybenzoate	
Aldehydes and ketones		Hydroxybiphenyl	
Dimethylformylbenzaldehyde		Dimethoxyacetylphenol	
Vinylmethoxybenzaldehyde		Dimethylpropenylphenol	
Trimethylformylbenzaldehyde		Hydroxystilbene	
Trimethoxybenzaldehyde		*Alcohol*	
2-Propylacetophenone		2-Benzofurylethanol	
Dimethylbenzofuranone			
Dimethyldihydrobenzopyranone			
Ethers			
Dimethoxyallylbenzene			
Methyldibenzofuran			
Bifuran			

[a] Peak numbers are those of compounds labelled in Fig. 1.

strong and very strong acid fractions)] and some organic acids in strong and very strong acid fractions. Finally, in addition to these families of which numerous components are isolated from slow pyrolysis oils (see the tables), some families are present but only some of their components are found in pyrolysis oils; these compounds are alcohols and lactones.

In the case of subfractions from basic fractions, the organic matrices are still too complex and our method of identification is inadequate.

CONCLUSIONS

The combination of ion-exchange chromatography and size-exclusion chromatography with coupled capillary GC–MS appears to be suitable for the analysis and the total characterization of pyrolysis oils. The strategy developed allows the accurate characterization of the volatile part of these pyrolysis oils, *i.e.*, about 70% of tars condensed during the pyrolysis. Moreover, this study indicates the efficiency of the functional sorting obtained by means of the improved API 60 technique.

However, the strategy is inadequate for the characterization of nitrogenous bases contained in the condensable tars from wood pyrolysis. Owing to the importance of these nitrogenous bases in relation to the environment, as a consequence of the mutagenic and carcinogenic characteristics of some of them, a new strategy is currently being developed.

REFERENCES

1 S. Kullaj, *Bull. Shkencave Nat.*, 38 (1984) 77.
2 E. M. Harris and B. A. A. Novaisah, *Proc Process Instrum. Meet.*, 10 (1978) 69.
3 M. P. Makhnev and N. I. Galkina, *Gidroliz. Lesokhim. Promst.*, 5 (1978) 29.
4 S. Kishimoto and K. Hirano, *Acta Aliment. Pol.*, 3 (1977) 237.
5 A. Y. Korol'kova and M. Z. Dubinoskii, *Gidroliz. Lesokhim. Promst.*, 3 (1977) 25.
6 P. P. Dikun, A. A. Liveroskii, E. I. Shmulevskaya, N. D. Gorelova, L. N. Parfent'eva and R. M. Vzdornikova, *Sovrem. Probl. Onkol.*, (1965) 48.
7 O. M. Yaropolova and D. V. Tishchenko, *Gidroliz. Lesokhim. Promst.*, 21 (1968) 11.
8 A. A. Liveroskii, E. I. Shmulevskaya, L. S. Romanovskaya, E. I. Pankina, V. N. Kun, P. P. Dikun and L. D. Kostenko, *Izv. Vyssh. Uchebn. Zaved. Lesn. Zh.*, 15 (1972) 99.
9 A. V. Rachinskii, N. M. Dorzet, L. M. Lavina, N. A. Chuprova, Z. P. Belikova, S. M. Repyakh, G. V. Nikolaeva, G. V. Tikhomirova and E. D. Levin, *Khromatogr. Anal. Khim. Drev.*, (1075) 249.
10 E. D. Levin and N. A. Chuprova, *Gidroliz. Lesokhim. Promst.*, 19 (1966) 14.
11 Y. K. Shposhnikov and L. V. Kosyukova, *Gidroliz. Lesokhim. Promst.*, 19 (1966) 19.
12 A. B. Wellburn and F. W. Hamming, *Nature (London)*, 212 (1966) 1364.
13 Z. O. Matveeka, *Tr. Lening. Lesotekh. Akad.*, 100 (1967) 343.
14 J. B. Luten, J. M. Ritskes and M. J. Wesseman, *Z. Lebensm.-Unters.-Forsch.*, 168 (1969) 289.
15 H. H. Brulin and G. Pensar, *Acta Chem. Scand.*, 19 (1965) 531.
16 I. I. Bardyshev, A. N. Bulgakov and A. L. Pertsovskii, *Khim. Prir. Soedin.*, 6 (1970) 539.
17 R. Ekman and G. Pensar. *Suom. Kemistiseuran Tied.* 80 (1971) 40.
18 B. Holmbom, *J. Am. Oil Chem. Soc.*, 54 (1977) 289.
19 D. Tishchenko, *Zh. Prikl. Khim.*, 31 (1966) 438.
20 S. Love and L. J. Bratzler, *J. Food Sci.*, 31 (1966) 218.
21 D. C. Elliott, *Final Report PNL 5943 UC-61D*, Pacific Northwest Laboratory, Richland, WA, 1986.
22 D. C. Elliott, in J. Soltes (Editor), (*ACS Symp. Ser.*, No. 376), American Chemical Society, Washington, DC, (1988), p. 55.
23 G. R. Rose, S. P. Singh, M. Onischak and S. P. Babu, *Energy from Biomass and Wastes*, IGT, Chicago, 1981, p. 613.
24 P. L. Desbène, D. Richard, D. C. Lambert, J. J. Basselier and R. Boulet, *Analusis*, 14 (1986) 148.
25 P. L. Desbène, D. C. Lambert, J. J. Basselier and R. Boulet, *Analusis*, 16 (1988) 478.
26 P. L. Desbène, D. C. Lambert, P. Richardin, J. J. Basselier, A. Y. Huc and R. Boulet, *Anal. Chem.*, 56 (1984) 313.
27 D. M. Jewell, in K. M. Altgelt and T. H. Oouw (Editors), *Chromatography in Petroleum Analysis (Chromatographic Science Series*, Vol. II), Marcel Dekker, New York, 1979, p. 275.
28 D. M. Jewell, J. H. Weber, J. W. Bunger, H. Plancher and D. R. Latham, *Anal. Chem.*, 44 (1972) 1391.
29 C. J. Collins, R. Triolo and M. H. Lietzke, *Fuel*, 63 (1984) 1202.
30 D. Meier, R. Doering and O. Faix, in W. Palz, J. Coombs and D. O. Hall (Editors), *Chromatographic Studies of Crude Oil from Wood, Energy from Biomass 3*, Elsevier, London, 1985, p. 732.
31 W. Schwald, R. Concin, G. Bonn and O. Bobletev, *Chromatographia*, 20 (1985) 35.
32 Y. E. Shen, C. V. Philip, R. G. Anthony and E. J. Soltes, *J. Chromatogr.*, 22 (1984) 497.