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Analysis of phenols in pyrolysis oils by gel permeation chromatography and multidimensional liquid chromatography

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Abstract

A simple method with minimal manual sample preparation was developed for the analysis of phenols in pyrolysis oils. Sample pre-treatment was done by gel permeation chromatography (GPC), where the high-molecular-mass lignins were separated from the phenols. Multidimensional liquid chromatography (LC–LC) was used in the analysis of the phenolic fraction. The pre-column was used for sample clean-up and pre-fractionation before introduction of the phenolic fraction to the analytical column. The repeatability and linearity of the total GPC and LC–LC methods were excellent. The results were in accordance with the reference method in which the sample pre-treatment was done by precipitating the lignins with water, and the phenols were extracted with toluene and analysed by GC–MS.

Keywords: Pyrolysis oils; Oils; Column switching; Sample preparation; Phenols

1. Introduction

Much attention has recently been paid to the use of pyrolysis oils as an alternative fuel for heat and power production and as a source of chemicals. Pyrolysis oils are usually produced from biomass, for example wood or peat, but also have been derived from waste [1]. Pyrolysis is carried out between 400 and 600°C and at near ambient pressure. Pyrolysis oils differ from the conventional fuel oils in many ways [2]. Water and oxygen content and density are all high. Because of the high water content, the heating values of the oils are relatively low. The several oxygen-containing compound groups, such as carboxylic acids, alcohols, aldehydes, ethers and phenols, make the oils relatively reactive. Especially the large amounts of formic and acetic acid and other carboxylic acids make them acidic and corrosive. Also, high-molecular-mass lignin-derived compounds are present in high concentrations. In contrast to petroleum-based fuel oils, the hydrocarbon content of the pyrolysis oils is fairly low.

The instability of pyrolysis oils creates problems in their use. A variety of reactions may take place during storage, transport and analysis. In addition, starting material and pyrolysis conditions have a marked effect on the properties of the final product, ensuring that the use of the pyrolysis oils is never straightforward. It is important, therefore, to know the exact composition of the oil to be used, and for this purpose new and efficient analytical methods are required for their chemical characterisation.

The complexity of pyrolysis oils makes their analysis a demanding task, and careful sample preparation is typically required. Pre-fractionation is almost always necessary, and complicated manual

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multi-step procedures are employed. The most commonly used sample pre-treatment techniques have been liquid–liquid extraction [3], adsorption chromatography by silica gel open-column chromatography [4] and, to a lesser extent, distillation [5]. Such procedures are time consuming, labour-intensive and expensive. In addition, losses of analytes are likely to occur in multi-step procedures. In traditional methods, the lignins are precipitated before the analysis by adding pyrolysis oil slowly to water [6]. Often, the analytes precipitate with the lignins, leading to erroneous results.

Fractions obtained from the pre-fractionation steps have typically been analysed by gas chromatography–mass spectrometry (GC–MS) [6,7], liquid chromatography (LC) or spectroscopic techniques [4]. Pyrolysis oils have also been analysed without any pre-fractionation, by chromatographic and spectroscopic techniques.

A number of methods have been developed for the analysis of conventional fuels. On-line coupled LC–GC has been used in the analysis of petroleum fuel products [8], while gel permeation chromatography (GPC)–GC has been used in the off-line analysis of pyrolytic tar [9] and the on-line analysis of coal liquids [10]. These methods cannot be adopted as such for the analysis of pyrolysis oils because of their different chemical composition. Relative to conventional oils, pyrolysis oils contain compounds with a wide range of volatilities and polarities and low solubilities in non-polar solvents, which restrict the use of GC analysis. In addition, the presence of compounds like lignin of high molecular mass may damage the GC column.

We have developed a method to analyse phenols in pyrolysis oils by GPC and multidimensional liquid chromatography (LC–LC). The whole sample is dissolved in tetrahydrofuran (THF) before injection into the GPC system for the pre-fractionation of the pyrolysis oils. High-molecular-mass lignins are separated from the phenols using THF as eluent. The phenol fraction is collected, concentrated by evaporation, and injected to a multidimensional reversed-phase (RP) liquid chromatographic system consisting of two columns of different selectivity. The first column is used for sample pre-fractionation and clean-up, after which the phenolic fraction is transferred to the analytical column for the final separation. Repeatability and linearity of the total method (GPC, LC–LC) were studied. The procedure is simple and allows analysis of the main phenolic compounds in the pyrolysis oils with minimal manual sample preparation.

2. Experimental

2.1. Chemicals and reagents

Acetonitrile (ACN) and THF were HPLC grade and were purchased from Lab Scan Analytical Sciences (Dublin, Ireland). The stabilised THF disturbed the detection, so unstabilised THF was used. Owing to peroxide formation it was used for only 1 month after opening of the bottle. Distilled water was deionised with a Water I system (Gelman Sciences, Ann Arbor, MI, USA). Catechol (99%), acetovanillone (98%), 2,4-dihydroxybenzaldehyde (98%), guaiacol (98%), 2,6-dimethylphenol (99%) and creosol (99%) were from Aldrich (Milwaukee, WI, USA), *m*-cresol (>98%), *o*-cresol (>99.5%) and vanillin (99%) from Fluka (Buchs, Switzerland); *p*-cresol (99%) from Sigma (Dorset, UK) and phenol (>99.5%) from Merck (Darmstadt, Germany).

2.2. Samples

Standard solutions of phenols were prepared in THF. Pyrolysis oil was produced by pyrolysing pine sawdust using a PDU-unit (20 kg/h) at the VTT Research Centre (Espoo, Finland). Before analysis the oil was diluted with THF to give a solution of 1% (w/w), this was dried with 3-Å molecular sieves and filtered to remove the solid char particles. It was necessary to remove the water in the sample because the GPC column could not tolerate water.

2.3. Gel permeation chromatography

THF was used as GPC eluent and was pumped at a flow-rate of 0.3 ml/min by a Jasco PU-980 pump (Tokyo, Japan). The injection valve was a six-port valve (Valco, Houston, TX, USA) equipped with an

injection loop having a volume of 24 μl. The column was a 250 mm×4.6 mm I.D. PLgel polymeric column containing styrene–divinyl benzene co-polymer (Polymer Labs., Shropshire, UK) packed with 5 μm particles of a pore size 50 Å. A similar PLgel column packed with particles of pore size 100 Å was tested. A Jasco UV detector Model UV-970 operating at a wavelength of 270 nm was used for detection.

2.4. Liquid chromatography

The liquid chromatograph was a Hewlett-Packard (Waldbronn, Germany) 1090 system. Data acquisition was performed by HP ChemStation for LC, Rev A.04.02. The injection valve was a Rheodyne 7010 six-port valve (Cotati, CA, USA) equipped with an injection loop having a volume of 50 μl. The pre-column was a 100 mm×2.1 mm I.D. Spherisorb cyano column (Phase Separations, Deeside, UK) packed with 5 μm particles. The analytical column was a 250 mm×4.6 mm I.D. Capcell Pak C_{18} column (Shiseido, Tokyo, Japan) packed with 5 μm particles of pore size 120 Å. The column switching valve was a manual six-port valve (Valco).

The eluent was a mixture of water and acetonitrile. The flow-rate of the eluent was 0.7 ml/min through the pre-column during clean-up and transfer, and 1 ml/min through the analytical column during the separation. The eluent composition was ACN–water (2:98, v/v) for the first 7 min (sample clean-up and transfer). After the valve was switched back to original position, the eluent composition was the same ACN–water (2:98, v/v) for the first minute. In the following gradient elution, the eluent composition was linearly changed from ACN–water (20:80, v/v) to ACN–water (55:45, v/v) during 28 min and finally linearly to 100% ACN during 8 min, where it was held for 5 min. A diode array detector operating at 210 nm and 270 nm was used for the detection.

2.5. Analytical procedure

The diluted sample was injected into the GPC system and the fraction containing the phenols was collected in a glass vial for further analysis with LC. The elution time of the phenolic fraction in GPC was

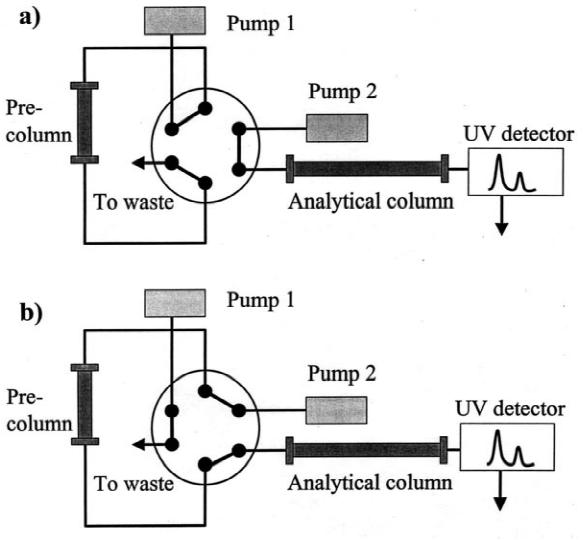

Fig. 1. Steps in column switching (LC–LC). Valve positions during (a) clean-up and pre-fractionation in the pre-column (0–0.5 min) and separation in the analytical column (6 min→), and (b) transfer of the phenolic fraction to the analytical column (0.5–6 min).

8–10 min and the volume of the fraction was 600 μl. The solution was concentrated to 200 μl with nitrogen flow at ambient temperature and 50 μl of the concentrated solution was injected into the LC system.

In the LC analysis the eluent was directed to waste for the first 0.5 min to remove the majority of matrix components (valve as in Fig. 1a). After the clean-up, the valve was switched and the phenolic fraction was transferred to the analytical column (Fig. 1b). The column switching valve was then switched back to the original position and the gradient elution was started (Fig. 1a).

2.6. Reference GC–MS method

The same pyrolysis oil has been analysed earlier with a GC–MS method [6,11]. The analytical procedure for the GC–MS analysis required sample pre-treatment in which the lignins were precipitated with water, after which the solution was filtered and the filtrate was extracted with toluene.

3. Results and discussion

3.1. Gel permeation chromatography

The choice of eluent was limited, because the eluent had to dissolve the pyrolysis oil and at the same time be compatible with GPC. Unlike conventional fossil fuel oils, pyrolysis oils are not soluble in non-polar alkanes, and not even in water, where the high-molecular-mass lignins are precipitated. Solvents in which the pyrolysis oil was soluble were THF, acetone and methanol. It was also possible to dissolve the pyrolysis oil first in THF and then dilute it with some medium-polar organic solvent such as ethyl acetate or dichloromethane. Accordingly, we chose a PLgel column with non-aqueous eluent for our studies. Of the solvents dissolving the pyrolysis oil, THF and ethyl acetate were compatible with the PLgel column. A pore size of 50 Å was chosen, because of the relatively small-molecular-mass lignins in the pyrolysis oil. No significant improvement in the resolution could be seen when a GPC column with pore size of 100 Å was tested at the front of a 50 Å column.

Both ethyl acetate and THF were tested as eluents. With the former, the pyrolysis oil was first dissolved in THF and then diluted in ethyl acetate. Even though ethyl acetate would have been more suitable for the following LC–LC separation, THF was chosen because it gave better separation of lignins and phenols.

Flow-rates between 100 μl/min and 300 μl/min were tested in GPC. The flow-rate had no significant effect on the resolution, and thus the highest flow-rate possible with the column was chosen to keep the analysis time as short as possible.

Study was made of the effect of the injection volume (1–50 μl) and concentration of the pyrolysis oil in THF. An injection volume of 24 μl and sample concentration of 1% (w/w) in THF were chosen for maximum sample capacity and resolution. GPC chromatograms of standard solution and pyrolysis oil are presented in Fig. 2.

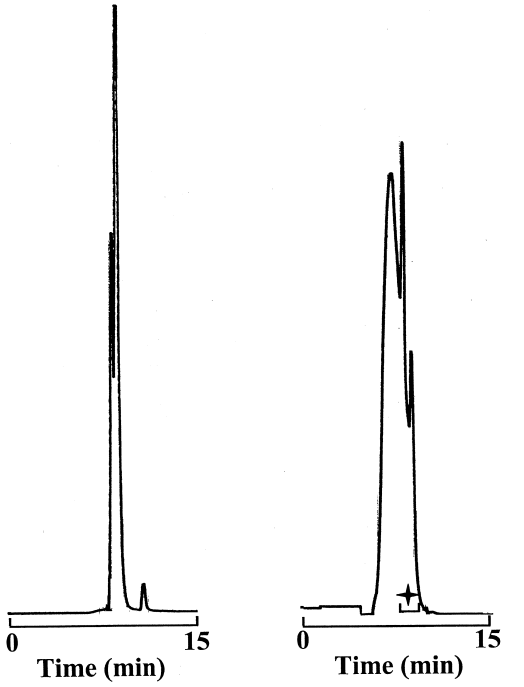

Fig. 2. GPC analysis of (a) phenol standard containing 30 μg/g eugenol, phenol, catechol, *o*-cresol and creosol in THF (scale 10 mV), and (b) 0.53% (w/w) pyrolysis oil in THF (scale 100 mV). The fraction containing phenols (8–10 min) is marked. The detection wavelength was 270 nm.

3.2. Liquid chromatography

The size of the phenol fraction eluted from GPC was 600 μl. As THF is a strong solvent in RPLC, injection of the whole GPC fraction into the RPLC column would have caused severe peak broadening. Peaks were fronting when the injection volume exceeded 50 μl but there was no fronting with an injection volume of 50 μl (Fig. 3a). Peaks were slightly sharper when the fraction was injected in a weak solvent, such as water.

The GPC fraction was concentrated by evaporation before injection into the LC system but evaporation to dryness could not be applied because the most volatile phenols were then partially lost. In addition, the peroxides present in THF would constitute a risk for explosition. Dilution of the phenol fraction in THF with water was also tested, but the peak shapes did not improve significantly.

A pre-column was used in LC for the final clean-up and pre-fractionation of the sample. A cyano column was chosen, because it provided different

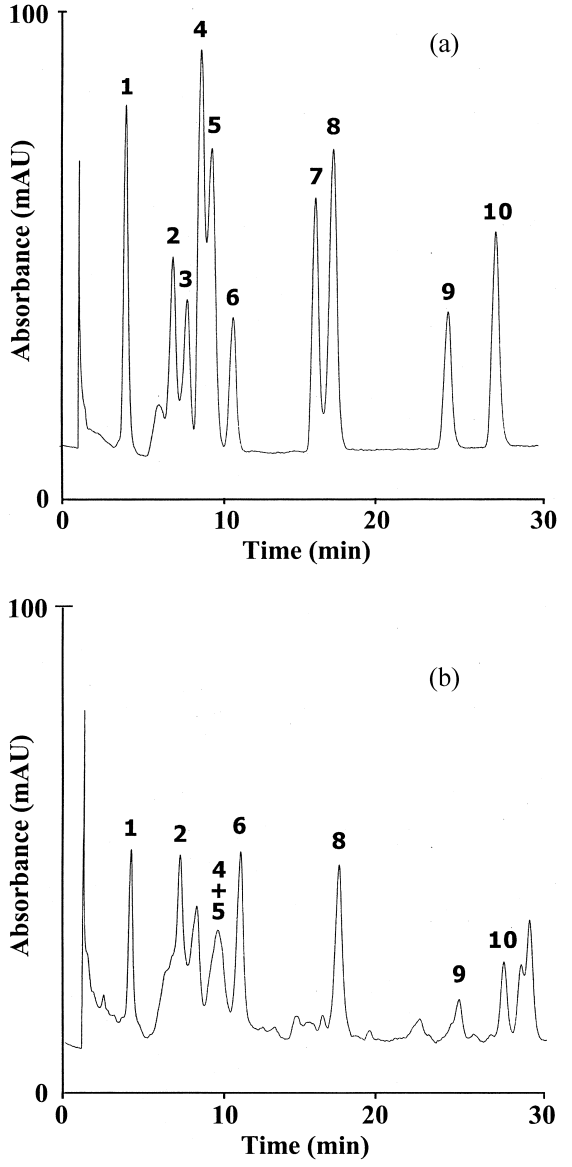

Fig. 3. LC–LC analysis of the GPC fraction of (a) 50 μg/g phenol standard in THF and (b) 1.23% (w/w) pyrolysis oil in THF. Peak numbers are explained in Table 1. The detection wavelength was 210 nm.

selectivity from the C_{18} analytical column and, unlike C_{18}, C_8 and phenyl columns, did not retain the phenols too strongly. The compounds eluted from the cyano column before the phenols were mostly carboxylic acids, which are ionised at neutral pH, and some other aliphatic compounds. The pre-column also protected the analytical column from some of the lignins remaining in the phenolic GPC fraction. As can be seen from Fig. 3b, the clean-up was effective because there are only a few additional peaks in the chromatogram. After the transfer of the phenolic fraction to the analytical column, the pre-column was cleaned by flushing with acetonitrile–water (50:50, v/v).

3.3. Quantitation

The applicability of the total method (GPC, LC–LC) for quantitative analysis was studied by evaluating the repeatability and linearity. In addition, the results obtained with the present method were compared with the results obtained with a reference method. The peak identification was done according to the retention times and UV spectra of the analytes and by applying the method of standard addition. The identification was reliable because three analytical separation steps (GPC, RPLC and RPLC) with different selectivities were employed.

The repeatabilities of retention times and peak areas with the standard mixtures were excellent, as can be seen from Table 1. Except for phenol, the linearity of the method was also very good (Table 1). Likewise for pyrolysis oils, the repeatabilities of retention times and peak areas were excellent (Table 2). The sensitivity of the total method was only satisfactory owing to the low sample capacity of GPC. The results obtained with the GPC and LC–LC methods were compared to the results of GC–MS analyses [6,11] and, as can be seen from Table 2 the values obtained with our method were better than those obtained with the GC–MS method. The probable reason for this is the losses of phenols due to co-precipitation with lignins in the sample preparation for the GC–MS method.

Because THF had to be used as eluent in GPC, slight peak broadening occurred in LC–LC, limiting the maximum injection volume. It also prevented on-line coupling of the GPC to the LC–LC system, which would have simplified the system and at the same time enhanced the sensitivity. As well, the peroxides present in THF disturbed the analysis and special attention had to be paid to the purity of the solvent.

Table 1
Relative standard deviations (RSDs) of the retention times and peak areas, and linearities in the range 10–220 μg/g (corresponding %, w/w, of 0.1–2.2 in pyrolysis oil) for standard samples[a]

Compound	RSD (%)				Linearity
	Retention time		Peak area		
	20 μg/g	100 μg/g	20 μg/g	100 μg/g	
1. Catechol	0.07	0.13	7.0	8.0	0.9987
2. Vanillin	0.06	0.07	5.8	7.3	0.9998
3. Acetovanillone	0.07	0.16	9.0	3.9	0.9999
4. 2,4-Dihydroxybenzaldehyde	0.18	0.10	5.6	2.5	0.9858
5. Phenol	0.17	0.16	5.4	2.4	0.8786
6. Guaiacol	0.06	0.05	11.6	4.3	0.9995
7. *m*-+*p*-Cresol	0.11	0.11	3.3	2.1	0.9998
8. *o*-Cresol+creosol	0.08	0.12	4.8	2.8	0.9996
9. 2,6-Dimethylphenol	0.08	0.16	6.8	2.8	0.9997
10. Eugenol	0.15	0.22	4.1	2.7	0.9998

[a] Results calculated from four replicate analyses (GPC, LC–LC).

Table 2
Relative standard deviations (RSDs) of the retention times and peak areas obtained with pyrolysis oil[a]

Compound	RSD (%)		GPC, LC–LC (%, w/w)	Reference method (%, w/w)[b]
	Retention time	Peak area		
1. Catechol	0.10	11.6	0.39	<0.01
2. Vanillin	0.10	16.3	0.43	0.11
4.+5. 2,4-Dihydroxybenzaldehyde+phenol	0.21	12.1	nq	–
6. Guaiacol	0.17	8.8	0.55	0.45
8. *o*-Cresol+creosol	0.22	4.1	0.40	0.56
9. 2,6-Dimethylphenol	0.22	7.7	0.07	–
10. Eugenol	0.25	7.9	0.12	0.02

[a] Results of the GPC, LC–LC method were compared with the results of the reference method [6,11].
[b] Lignins precipitated with water, phenols extracted with toluene, GC–MS analysis.
nq=Not quantified because of the co-elution of the peaks.

4. Conclusions

The GPC and LC–LC method developed for the analysis of phenols in pyrolysis oil was repeatable and linear. Only minimal manual sample preparation was required, and the time needed for one analysis was shorter than with the previous GC–MS method. Clean-up of the sample was effective due to the different selectivities in the three separation steps, and there were only a few interfering peaks in the LC chromatogram of pyrolysis oil. The results were in accordance with the results obtained by the GC–MS method but with less loss of analytes.

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