

Isolation of the phenolic fraction of coal pyrolysis tars by ion-exchange chromatography

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ABSTRACT

The isolation of the phenolic fraction from coal pyrolysis tars by ion-exchange chromatography is reported. Tars were obtained from low temperature pyrolysis (600°C) of four coals varying in rank from lignite to bituminous. The phenolic fraction was extracted from tars using an anion-exchange resin (Amberlyst A-26, OH-form) activated by consecutive treatments in a column with 2 M HCl, 2 M NaOH and isopropanol–water (1:1). Tar samples dissolved in dichloromethane–diethyl ether (5:1) were shaken with the resin (10 cm³/g sample) for 30 min. The resin was then separated by filtration and the acid fraction was quantitatively eluted from the resin with chlorotrimethylsilane–dichloromethane. The acid fraction extracted in this way represented between 46 and 58% (w/w) of the whole tar for the analysed samples. The efficiency of the separation was tested by enthalpimetric titration, gas chromatography, Fourier transform (FT) IR spectroscopy and ¹H NMR. The residual fraction obtained after removal of the acid fraction has no acid character and does not contain hydroxyl groups. In contrast, phenolic structures are concentrated in the acid fraction. The main compounds in the acid fraction were identified and quantified by wide-bore gas chromatography using external standards. Several structural parameters of the fractions were deduced from FT-IR and ¹H NMR data. The acid fraction is mainly aromatic in nature whereas the aliphatic structures tend to concentrate in the residue.

INTRODUCTION

Coal-derived liquids (CDLs) are complex mixtures of widely varying, predominantly aromatic compounds. The development of coal conversion processes such as liquefaction and pyrolysis has created the need for analytical methodologies of fractionation and characterization of CDLs to understand conversion mechanisms.

The fractionation of CDLs is usually carried out by distillation, solvent extraction or by chromatographic methods based on sorption, steric exclusion or ion-exchange processes. Separation methods and the characterization of CDLs have been reviewed by Poirier and George [1]. The development of non-aqueous ion-exchange resins has initiated the development of separation schemes for CDLs into discrete compound classes giving fractions based on chemical functionality differences (acids, bases and neutral compounds) [2–5].

Tars from the low temperature pyrolysis of coal

have a large content of phenolic compounds especially when low rank coals are processed. This acid fraction is useful as a chemical feedstock but it is undesirable when CDL are used to produce synthetic fuels. Therefore fractionation schemes which allow an easy and large scale separation of the phenolic fraction are required.

Fractionation of pyrolysis tars by ion-exchange chromatography (Amberlyst A-27 and A-15) followed by extrography of the neutral fraction according to the separation scheme of Strachan and Johns [5] has been carried out with unsatisfactory results [6]. Loss of material and the presence of hydroxyl groups in basic and neutral fractions were found. Zanella has reported [7] satisfactory results for the separation of the phenolic fraction of low temperature tars using Amberlyst A-26 and batch procedures instead of column chromatography. This procedure simplifies the fractionation schemes proposed by other workers and can be applied on a large scale to isolate the acid fraction of tars for character-

ization and use as chemical feedstocks or for upgrading CDLs.

In this work the isolation of the acid fraction of low temperature pyrolysis tars using an anion-exchange resin (Amberlyst A-26) was studied. Four tars obtained from coals varying in rank from lignite to bituminous were fractionated and the phenolic fractions obtained were characterized by enthalpic titration, gas chromatography and spectroscopic techniques [Fourier transform (FT) IR and ^1H NMR].

EXPERIMENTAL

Starting materials

Tars were obtained from the low temperature pyrolysis of four coals varying in rank: a brown coal (Mequincza), two subbituminous coals from Teruel (AA1, EL3) and a bituminous coal from Asturias (Hu). Pyrolysis was carried out in a fluidized bed at 600°C under nitrogen and tars were extracted with dichloromethane which was then removed by distillation.

Ion-exchange separation

The resin used was Amberlyst A-26 (Fluka, Buchs, Switzerland), a strong anion-exchange resin which was carefully activated to prevent artifacts arising from the incorrect preparation of non-aqueous ion-exchange resins [8]. A column (50 × 2 cm I.D.) packed with 100 g of the resin was eluted with 2 M HCl (2 l) and distilled water until free of chloride ions. It was subsequently activated by washing with 2 M NaOH (2.5 l) followed by distilled water until a neutral pH was reached and then isopropanol–water (1:1; 2.5 l).

Finally the resin was conditioned by Soxhlet extraction with isopropanol (24 h) and then diethyl ether (24 h). The resin was stored in diethyl ether to prevent absorption of CO₂.

The tar sample was dissolved in a mixture of dichloromethane–diethyl ether (5:1, v/v) in a ratio of 60 ml/g sample. The solution was treated with the resin (10 ml/g sample) in an Erlenmeyer flask and the system mechanically shaken for 30 min. The resin was separated from solution by filtration and then washed with dichloromethane until colourless washings were seen. These washings were combined with

the non-retained solution and the solvent was eliminated by distillation. This residue consists of the basic and neutral fractions of tar.

The acid fraction was recovered from the resin by treating in a flask with a solution of chlorotrimethylsilane (Aldrich Chemie) in diethyl ether ($1.8 \cdot 10^{-4}$ M) for 30 min. The resin was then washed with dichloromethane until a colourless liquid was obtained. For tars with high contents of phenol compounds it may be necessary to repeat the elution process. Solvents were then removed by distillation.

Analytical methods

Elemental analyses (C, H, N, S) were carried out using Leco (St. Joseph, MI, USA) elemental analysers (CHN-600, SC-32). The amount of phenolic compounds in various fractions was determined by enthalpic titration according to the following procedure [7].

The sample (0.1–0.3 g) was dissolved in anhydrous acetone (100 ml) and accurately titrated with KOH (0.5 M) in isopropanol. The end-point was indicated by an increase in temperature of 2°C, which was detected by a thermocouple. The KOH solution was previously titrated with acetic acid. The standard deviation (σ) found for this method was $1 \cdot 10^{-4}$ for model compounds (phenols) and $1 \cdot 10^{-2}$ for tars from different coal pyrolysis processes.

Gas chromatography (GC) of tars and their fractions was carried out on a Varian 3400 system (Walnut Creek, CA, USA) using a wide-bore (0.53 mm, 25 m) CP Sil 5B wall-coated column from Chrompack (Middelburg, Netherlands). The chromatographic conditions are given in Fig. 1. GC–mass spectrometry (MS) was carried out on a Varian 3300 system linked to a Finnigan ion trap detector (ITD 800; San Jose, CA, USA). The chromatographic conditions were the same than those used for GC unless a splitless injection mode was used. The National Bureau of Standards (USA) computerized library was used for identification.

^1H NMR spectra of tars were obtained in a Bruker (Karlsruhe, Germany) WP80 CW system, 80 MHz, with samples solved in C²HCl₃ using trimethylsilane (TMS) as a reference. FT-IR spectra were determined on a Nicolet 10 DX instrument (Madison, WI, USA) with tars on KBr windows.

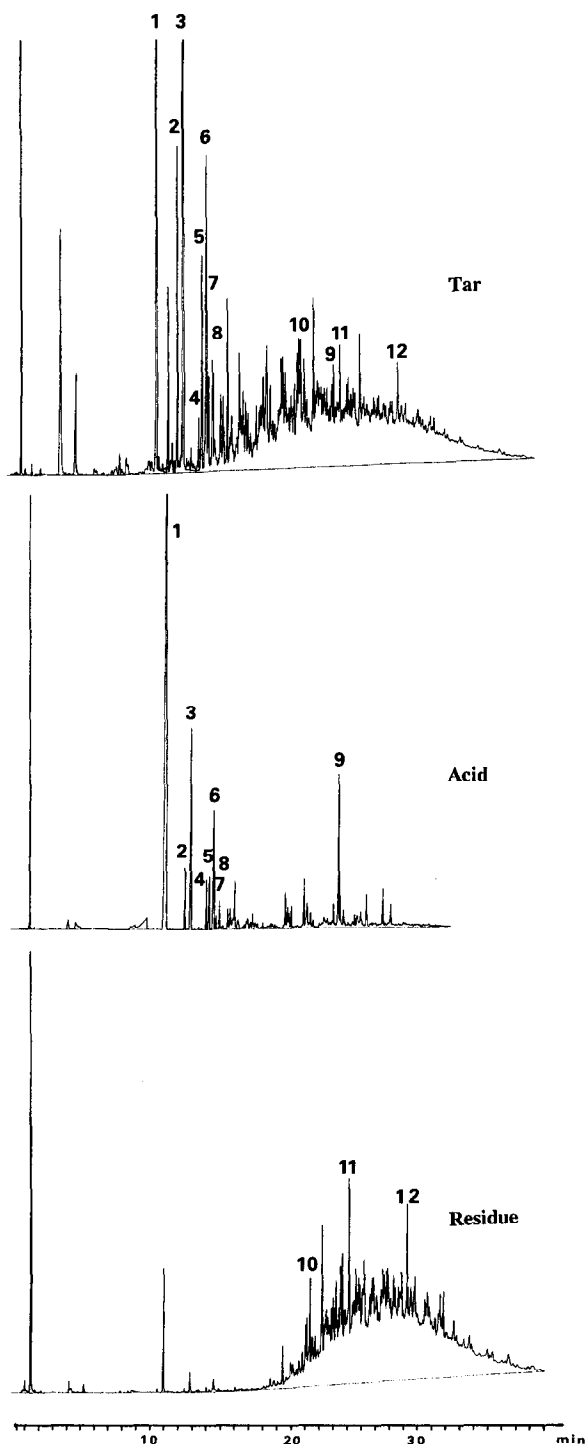


Fig. 1. Gas chromatograms of the tar, acid fraction and residual fraction from AA1 coal. Column, 0.53 mm \times 25 m, CP Sil 5B WCOAT; sample, $1 \cdot 10^{-6}$ l, split, 1:30; detector, flame ionization; temperature, 350°C; injector, 350°C; temperature programme, 50°C, 5 min hold, 10°C/min to 300°C; carrier gas, helium. Peaks 1–9 are identified in Table II. Peak 10 = *n*-C₁₆; 11 = *n*-C₁₈; and 12 = *n*-C₂₂.

RESULTS AND DISCUSSION

Table I shows the main characteristics of the starting tars and their acid and residue fractions. The important contribution of the acid fraction, which represents the 50% or more of the tar, is noted. Losses less than 0.1 wt% were found in all instances.

The phenolic content of tars, determined by enthalpimetric titration, tends to increase with increasing rank of the starting coals. However, it remains constant, in practice, in all acid fractions independent of the origin of the tar. No acid functions were found in the residue (basic plus neutral) by enthalpimetric titration. The elemental analysis data show that the oxygen contained in tars is mainly recovered in the acid fraction, so that the oxygen content of the residue is low. This fact could be used for upgrading liquids from low quality coals.

Gas chromatography

Fig. 1 shows the chromatograms obtained for the whole tar and the acid and residual tar fractions. It is noted that the chromatogram of the whole tar splits into two chromatograms corresponding to the acid and the residual fractions. Peaks that correspond to the lightest phenolic compounds appear in the acid fraction and not in the residual fractions, with the exception of the phenol (0.35%, w/w, in the residual fraction against 52.32% (w/w) in the acid fraction). On the other hand, the peaks with longer elution times appear in the residual fraction and not in the acid fraction, with the exception of anthracene (6.58% in the acid fraction).

Peaks in the acid fraction have been identified by their relative retention times (RRT) referred to phenol. A set of external standards was used for identification. A difference ≤ 0.005 between the RRT of the standard and the identified peak was accepted.

Peak abundances were calculated from the normalized areas of peaks which were corrected by a relative response factor according to the equations:

$$A_i = NA_i \cdot RRF_i \quad (1)$$

$$RRF_i = RF_i / (RF)_{\text{phenol}} \quad (2)$$

$$RF_i = \frac{\text{mass of external standard}}{\text{peak area}} \quad (3)$$

$$(\text{Abundance})_i (\%) = \frac{A_i}{\sum A_i} \times 100 \quad (4)$$

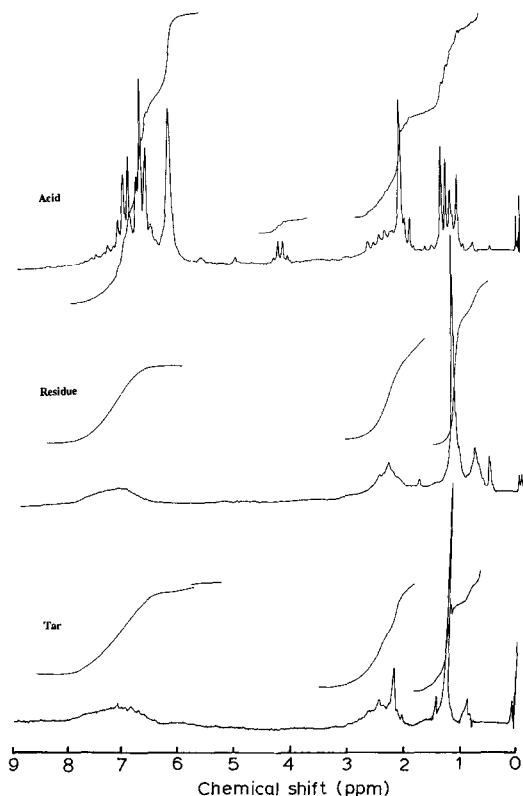


Fig. 2. ^1H NMR spectra of tar Hu and its fractions.

and their fractions evaluated by ^1H NMR. Spectra were divided for integration in specific zones according to Stoppel and Bartle [9] and Ibarra *et.al.* [10]. It is observed that the acid fraction has a higher aromatic hydrogen content than the starting tar in all instances whereas the residue is more aliphatic. The variation of the aromatic to aliphatic hydrogen ratio ($H_{\text{ar}}/H_{\text{al}}$) reflects this trend. The higher hydrogen content in the phenolic structures of the acid fraction is also revealed by ^1H NMR (Fig. 2 and Table III). Owing to the high sensitivity of the chemical shift of phenolic protons to experimental conditions (such as concentration and solvent) NMR has not been used for quantitative purposes.

FT-IR spectroscopy

Fig. 3 shows the FT-IR spectra of the whole tar, the acid and the residue fractions corresponding to sample AA1. Similar spectra were obtained for the

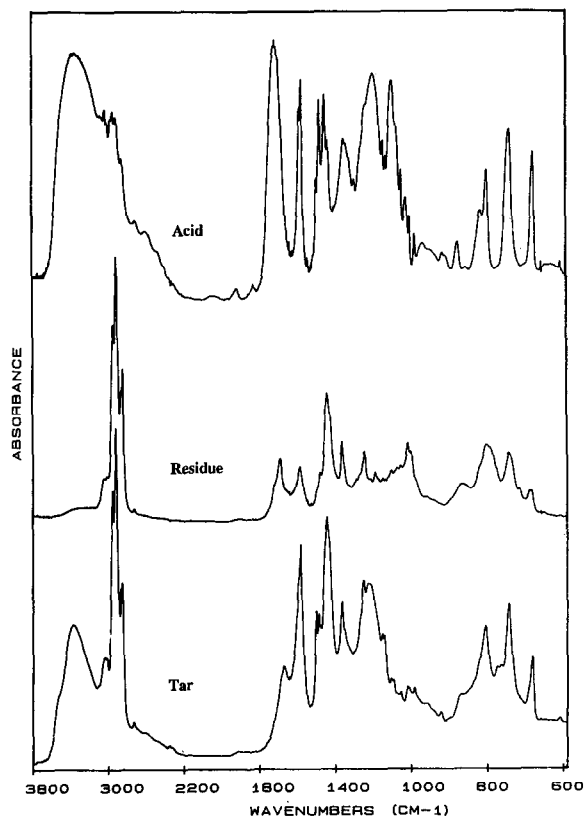


Fig. 3. FT-IR spectra of tar AA1 and its fractions.

other samples. The total disappearance of the hydroxyl band (3375 cm^{-1}) in the residue after the acid fraction removal from tar can be seen. The acid fraction has a markedly increased content of phenolic compounds (3375 and 1124 cm^{-1}), other acidic groups such as $\text{C}=\text{O}$ (1734 and 1225 cm^{-1}) and aromatic structures (several bands at 1600 and 1500 cm^{-1}). The residue shows, in addition to the disappearance of hydroxyl bands, a higher aliphatic character than the tar and the persistence of $\text{C}=\text{O}$ structures (1685 cm^{-1} , aromatic ketones and quinones). This band should be related to the presence of polar structures in the residue [2,11].

Fig. 4 shows expanded FT-IR spectra corresponding to aliphatic and aromatic zones of tar AA1 and its fractions. The appearance in the acid fraction of two aromatic hydrogen bands at 3054 cm^{-1} (benzenic structures) and 3020 cm^{-1} (more condensed aromatic structures) can be observed, which

TABLE III
HYDROGEN DISTRIBUTION (%) FOR TARS AND THEIR FRACTIONS

H_r = ring-joining methylene; H_z = CH₃, CH₂ and CH α to an aromatic ring; H_n = CH₂ and CH β to an aromatic ring (naphthenic); H _{β} = β -CH₃, CH₂ and CH γ or further from an aromatic ring; H _{γ} = CH₃ γ or further from an aromatic ring.

Type of hydrogen	Hydrogen concentration (ppm)	Mequinenza			AA1			EL3			Hu		
		Tar	Acid	Residue	Tar	Acid	Residue	Tar	Acid	Residue	Tar	Acid	Residue
H _{ar}	9.0	26.0	39.5	20.1	36.3	39.5	24.4	36.3	39.7	27.9	26.6	41.8	21.2
H _{on}	6.5	5.5	9.1	—	5.7	9.1	—	5.2	10.6	—	3.1	16.9	—
H _r	4.5-3.3	—	1.8	—	—	1.8	—	—	—	—	—	3.0	—
H _z	3.3-2.0	30.1	22.3	28.3	30.0	22.3	34.6	31.5	18.2	29.5	34.7	16.9	24.6
H _n	2.0-1.6	8.3	4.1	11.0	4.6	4.1	4.7	4.5	5.0	6.2	3.0	4.2	5.9
H _{β}	1.6-1.0	19.5	15.9	32.7	14.4	15.9	23.5	15.5	16.6	27.9	26.5	15.4	38.1
H _{γ}	1.1-0.5	10.2	7.3	7.9	10.0	7.3	12.8	7.0	8.9	8.5	6.1	1.8	10.2
H _{ar} /H _{al}		0.38	0.8	0.25	0.6	0.8	0.32	0.62	0.82	0.4	0.4	1.1	0.3

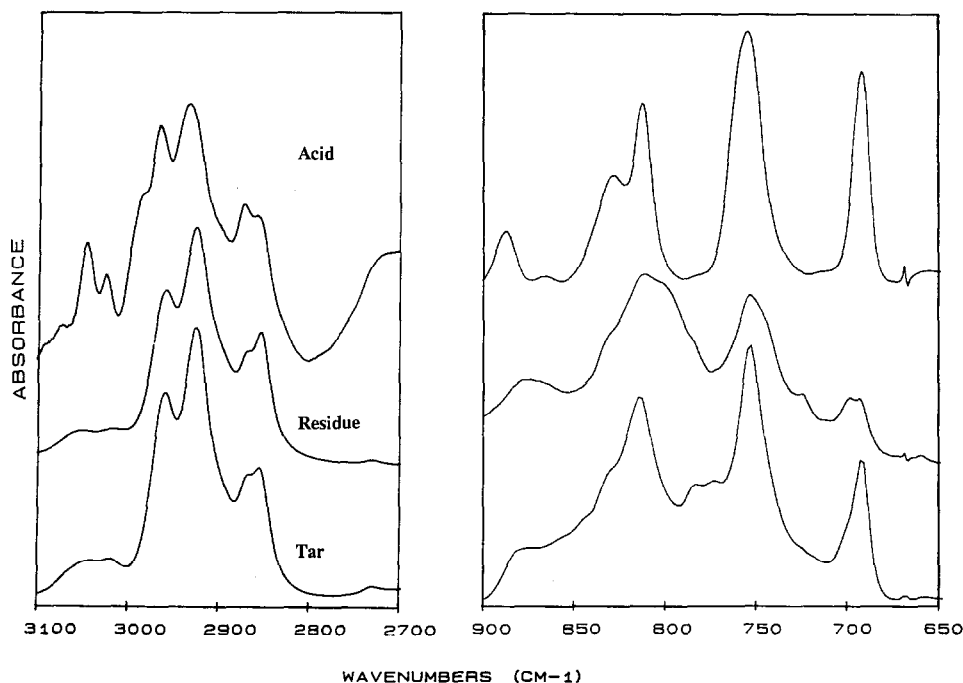


Fig. 4. Expanded spectra in the aliphatic and aromatic zone of tar AA1 and its fractions.

denotes its higher aromatic character in relation to the starting tar. The increase in the acid fraction of the 690 cm^{-1} band (monosubstituted aromatic structures) and the 825 and 890 cm^{-1} bands (more substituted aromatic rings) also confirms this fact. Likewise the increase in the 2960 and 2870 cm^{-1} bands (asymmetric and symmetric CH_3 stretching modes) in relation to the band at 2924 and 2856 cm^{-1} (asymmetric and symmetric CH_2 stretching modes) indicates shorter aliphatic chains for the acid fraction and thus a lower aliphatic character.

Evidence for the confirmation of these facts will be deduced from the structural parameters presented in the following section.

Structural parameters

On the basis of the elemental analysis and $^1\text{H-NMR}$ data some structural parameters as defined by Brown and Ladner [12] can be easily deduced according to the following equations:

$$f_a = 1 - C_{al}/C \quad (5)$$

where f_a is the aromaticity or aromatic carbon

content and C_{al} the carbon in aliphatic structures which calculated from the eqn. (6):

$$C_{al}/C = (H_{al}/H) \cdot (H/C)/(H_{al}/C_{al}) \quad (6)$$

where H_{al}/H is the fraction of total hydrogen present as aliphatic hydrogen, H/C is the atomic hydrogen to carbon ratio calculated from elemental analysis and H_{al}/C_{al} is an atomic hydrogen to carbon ratio for aliphatic chains which is generally taken to be 2.3 for tars derived from coal [13]. H_{al} is usually derived from NMR or FTIR data [14]. In this paper H_{al} (H_x , H_β , H_γ) has been calculated using the H_{ar}/H_{al} ratio deduced from $^1\text{H-NMR}$ data and the following equation:

$$H_T = H_{al} + H_{ar} + H_{acid} \quad (7)$$

where H_T is the total hydrogen content determined by elemental analysis and H_{acid} is the hydrogen in acid structures determined by enthalpimetric titration. The H/C ratio has also been corrected for the hydrogen in acid structures.

The results obtained in this way are shown in Table IV. It can be observed that the aromatic

TABLE IV
STRUCTURAL PARAMETERS OF TARS AND THEIR FRACTIONS

Sample	Fraction	H/C	H _{ar} /H _{al}	H _{al} (%, w/w)	H _{ar} (%, w/w)	H _{al} /H	C _{al} (%, w/w)	C _{ar} (%, w/w)	f _a	H _{ar} /C _{ar}
Mequinenza	Tar	1.18	0.38	5.36	2.03	0.73	27.9	47.4	0.63	0.51
	Acid	1.10	0.79	3.49	2.75	0.56	18.4	49.6	0.73	0.67
	Residue	1.32	0.25	6.79	1.70	0.80	41.8	35.6	0.54	0.57
AA1	Tar	1.10	0.61	4.47	2.73	0.62	23.5	55.0	0.70	0.60
	Acid	1.09	0.80	3.78	3.02	0.56	19.6	55.6	0.74	0.65
	Residue	1.19	0.32	6.04	1.93	0.76	31.4	49.2	0.61	0.47
EL3	Tar	1.06	0.62	4.23	2.63	0.62	22.6	55.3	0.71	0.57
	Acid	1.15	0.82	3.92	3.22	0.55	20.1	54.5	0.73	0.71
	Residue	1.27	0.39	6.34	2.47	0.72	33.2	49.8	0.60	0.59
Hu	Tar	1.12	0.38	5.53	2.10	0.72	28.6	53.0	0.65	0.48
	Acid	1.13	1.09	3.34	3.65	0.48	17.8	56.3	0.76	0.78
	Residue	1.30	0.27	7.32	1.98	0.79	38.8	47.4	0.55	0.50

hydrogen and carbon content of the acid fraction increased in all instances in relation to the whole tar and the residue. The acid fraction also has a higher aromaticity (f_a). Whereas the residue has a higher aliphatic character. The degree of aromatic substitution evaluated from the aromatic hydrogen to aromatic carbon ratio (H_{ar}/C_{ar}) denotes a lower degree of substitution for the acid fraction.

CONCLUSIONS

The acid fraction of low temperature pyrolysis tars can be successfully separated by ion-exchange chromatography on Amberlyst A-26 and later elution with chlorotrimethylsilane. Hydroxyl groups have not been detected by FT-IR and enthalpimetric titration in the residual fractions, although some aromatic compounds have been detected in the acid fraction. The acid fraction represents 50% or more of all studied samples. It has a higher aromatic character than the original tar whereas the aliphatic structures tend to be concentrated in the residue. An important removal heterograms (O + S) from the tar can be achieved by the separation of the acid fraction.

REFERENCES

- 1 M. A. Poirier and A. E. George, *Energy Sources*, 5 (1981) 339.
- 2 P. V. Webster, J. N. Wilson and M. C. Franks, *Anal. Chem. Acta*, 38 (1967) 193.
- 3 S. E. Scheppele, P. A. Benson, G. J. Greenwood, Q. Grindstaff, T. Aczel and B. Bieber, *Prepr. Am. Chem. Soc. Div. Petroleum Chem.*, 24(4) (1979) 963.
- 4 J. B. Green, R. J. Hoff, P. W. Woodward and L. L. Stevens, *Fuel*, 63 (1984) 1920.
- 5 M. G. Strachan and R. B. Johns, *Anal. Chem.*, 58 (1986) 312.
- 6 A. C. Gracia, *Degree dissertation*, University of Zaragoza, Zaragoza, 1987.
- 7 I. Zanella, *Ph. Thesis*, University of Metz, Metz, 1987.
- 8 M. G. Strachan and R. B. Johns, *Anal. Chem.*, 59 (1987) 636.
- 9 Z. Stonpel and K. D. Bartle, *Fuel*, 62 (1983) 900.
- 10 J. V. Ibarra, I. Cervero and R. Moliner, *Fuel Process. Technol.*, 22 (1989) 135.
- 11 J. V. Ibarra, R. Moliner and A. C. Gracia, presented at the *XVII Meeting on Chromatography and Related Techniques, Reus, November 1989*.
- 12 J. K. Brown and W. R. Ladner, *Fuel*, 39 (1960) 87.
- 13 C. Snape, W. R. Ladner and K. D. Bartle, in H. D. Schultz (Editor), *Coal Liquefaction*, Wiley, New York, 1984, Chapter 4.
- 14 J. V. Ibarra and R. Moliner, *J. Anal. Appl. Pyrol.*, 20 (1991) 171.