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Quantitative structure-type analysis of heterocompound–hydrocarbon mixtures

VI. Characterization of the nature of neutral heterocompounds in a product of brown coal refining

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ABSTRACT

Neutral heterocompounds are one of the major fractions of the pyrolysis or hydrogenation products of brown coals. They are classified into two groups by chromatographic methods. The first group (thiophenes, aliphatic ketones) elutes from the normal phase with non-polar eluents, in analogy with aromatic hydrocarbons. They can be separated from aromatic hydrocarbons by complex formation with palladium chloride [*Fuel*, 65 (1986) 270–273; *J. Chromatogr.*, 509 (1990) 27–32]. The second group elutes from the normal phase with polar eluents. The neutral heterocompounds in an extract of heat-pretreated brown coal were separated by semipreparative high-performance liquid chromatography. They were fractionated by increasing polarity and subsequently characterized by Fourier transform infrared spectrometry, protonnuclear magnetic resonance and mass spectrometry. Results fo these spectrometric methods (*i.e.* the existence of hydroxy and carbonyl residues) could be verified by derivatization with 2,4-dinitrophenylhydrazine and 3,5-dinitrobenzoylchloride followed by qualification of these derivatives by reversed-phase chromatography. The neutral heterocompounds were hydrogenated in two steps, and the resulting hydrocarbons were characterized by semipreparative and analytical high-performance liquid chromatography, as well as by capillary gas chromatography. General conclusions about the structures, as result of the combination of the different applied methods, could be made.

INTRODUCTION

The refining of brown coals by thermal or hydrogenating processes leads to products such as tars and hydrogenation products. In addition to extracts of heat-pretreated brown coals, such products include hydrocarbons (saturated and aromatic) and heterocompounds (acidic, basic and a significant fraction of neutral compounds).

The characterization of the composition of such refined and pretreated brown coals is necessary for the elucidation of the reaction mechanisms that occur during the processing. The development of an on-line semipreparative high-performance liquid

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chromatography (HPLC) method for the structure-type analysis of heterocompound–hydrocarbon mixtures and its application to the characterization of technical products of thermal and hydrogenated refined brown coals and to mineral oil processing and the reactions taking place during these processes have reported in previous papers [1–4]. The chromatographic properties of the neutral heterocompounds (NHC) are determined by their polarity. The less polar NHC (thiophenes, alkanones) elute from precolumn 1, packed with a normal-phase silica support, together with aromatic hydrocarbons, with non-polar eluents (*n*-hexane, *n*-pentane). They are separated by complex formation of the NHC on palladium chloride [5] on precolumn 2. This on-line separation (Fig. 1) has been described by Zobel *et al.* [6]. The NHC with higher polarity elute from precolumn 1 with mixtures of polar and non-polar aprotic eluents or polar aprotic eluents. These compounds are either thermally unstable or have an increased boiling point. It is not possible to characterize the individual compounds by capillary gas chromatography (cGC) coupled with mass spectrometry (MS). Spectrometric methods for the characterization of the NHC provide only circumstantial evidence for the existence of functional or structural groups.

EXPERIMENTAL AND RESULTS

Separation and characterization of NHC in extracts of heat-treated brown coal

Separation and structure-type analysis in the extract. The structure-type composition of the extract of heat-treated brown coal (referred to as sample 1) was determined by semipreparative HPLC (Fig. 1) by the method of Zobel and co-workers [1–4,6].

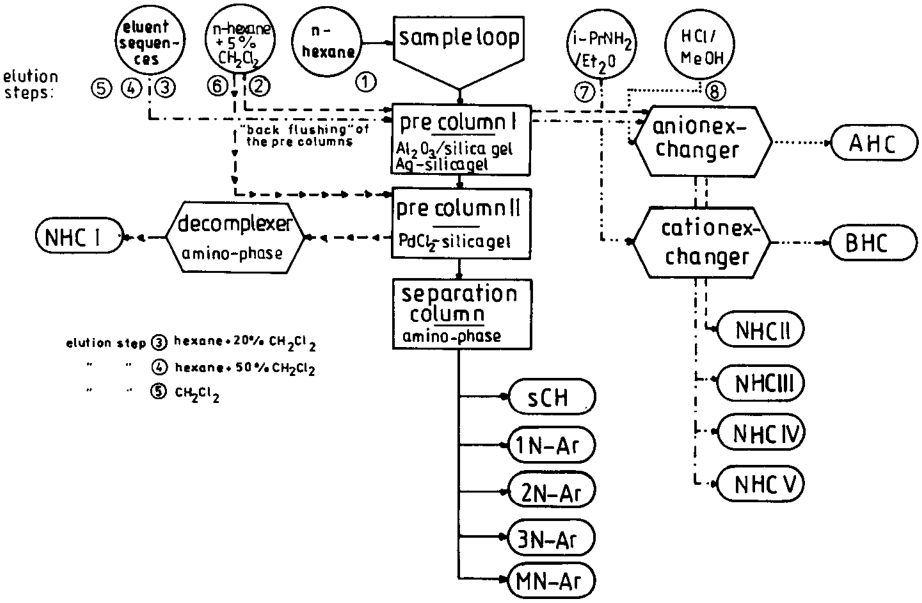


Fig. 1. Scheme of the structure-type separation.

TABLE I

STRUCTURE-TYPE CHARACTERISTICS OF AN EXTRACT OF HEAT-PRETREATED BROWN COAL

Structure type	Content (%)	Qualitative composition
sCh	24.9	Paraffins, olefines
1 N-Ar	5.9	Alkylbenzenes, tetralenes/indanes
2 N-Ar	5.3	Naphthalenes, acenaphthenes, diphenyls, fluorenes
3 N+MN-Ar	3.7	Antracenes, phenathrenes, pyrenes, chrysenes, polycyclic aromatics
NHC I	10.3	Homologous series of alkanones, dibenzothiophenes
NHC II	3.9	
NHC II	4.2	
NHC IV	8.8	
NHC V	18.3	
BHC	2.3	
AHC	8.4	

Backflushing of precolumn 1 was performed with the following eluent sequences: *n*-heptane–dichloromethane 9:1 (NHC II), *n*-pentane–dichloromethane 8:2 (NHC III), *n*-pentane–dichloromethane (NHC IV) and dichloromethane (NHC V). The structure-type composition which was found in sample 1 is listed in Table I. The following abbreviations are used in the table and throughout the whole paper: sCH, saturated hydrocarbons; *x* N-Ar cyclic hydrocarbons, where *x* indicates the number of ring systems; BHC, basic heterocompounds; and AHC, acidic heterocompounds.

The qualitative composition of the hydrocarbons and NHC I fractions was deduced from the HPLC (Fig. 2A and B) and the cGC–MS profiles. The fractions NHC I–NHC V were characterized by Fourier transform infrared (FT-IR) spectrometry, proton nuclear magnetic resonance (^{1}H-NMR) and MS.

Interpretation of the FT-IR spectra. The FT-IR spectra of the NHC II and NHC V fractions suggest the existence of OH residues (band at 3450 cm^{-1}) and C=O residues (band at 1700 cm^{-1}) in all NHC fractions and C–O–C residues (band at 1700 cm^{-1}). In the NHC I fraction an intensive band at 2930 cm^{-1} was found, suggesting aliphatic CH_2 residues. This band was very weak in the NHC V fraction (Fig. 3). The intensities of the bands at 1600 and 3080 cm^{-1} increased with the polarity of the NHC.

Interpretation of the ^{1}H-NMR spectra. From the ^{1}H-NMR spectra, the characteristics of H_{ar} (hydrogen in aromatic structures), H_α (hydrogen in the α-methyl group on aromatic rings), H_β (hydrogen in the β-methylene group of aliphatic residues and naphthenic methylene groups), as well as H_e (hydrogen in the terminal methyl group of aliphatic residues) could be deduced (Table II).

Interpretation of the mass spectra. Electron ionization mass spectra of the NHC I and NHC V fractions by 70 eV are shown in Fig. 4a and b. Fragments of aliphatic chains were found in both mass spectra (mass numbers 29, 43, 57, 71, 85, 113 and 127; see also ref. 7). In the spectrum of the NHC I fraction larger alkyl chains dominate. The fragment with mass number 18 in the NHC V fraction shows the existence of OH residues on aliphatic or naphthenic structures. Fragments of aromatic structures

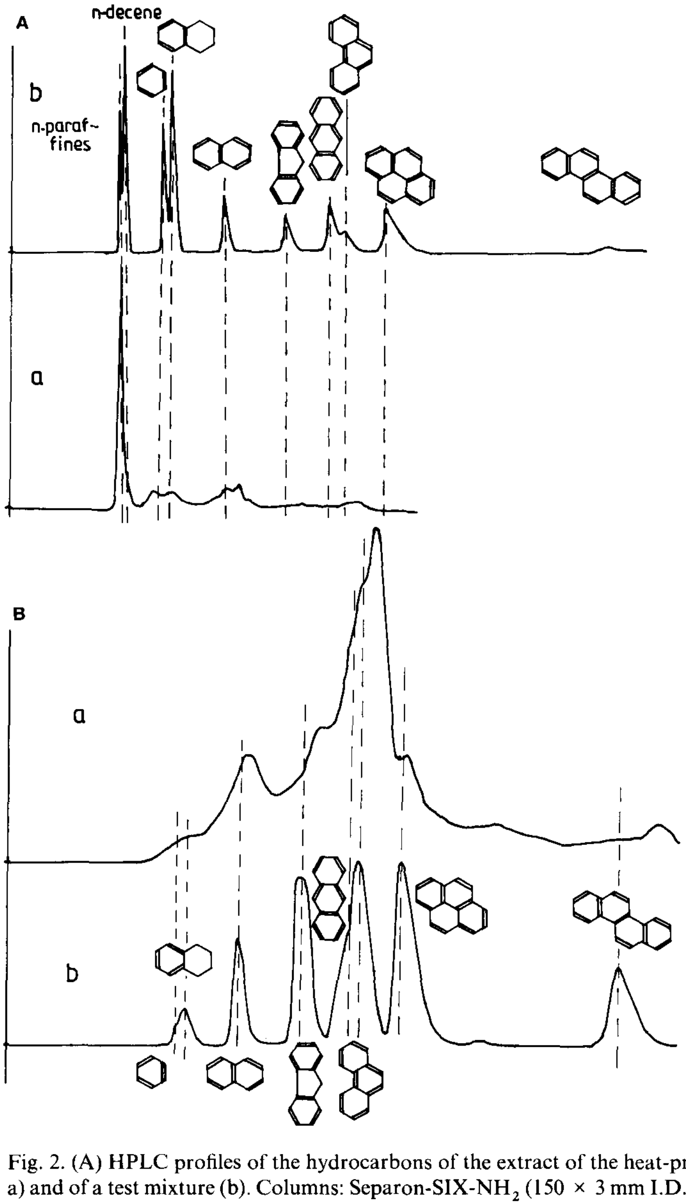
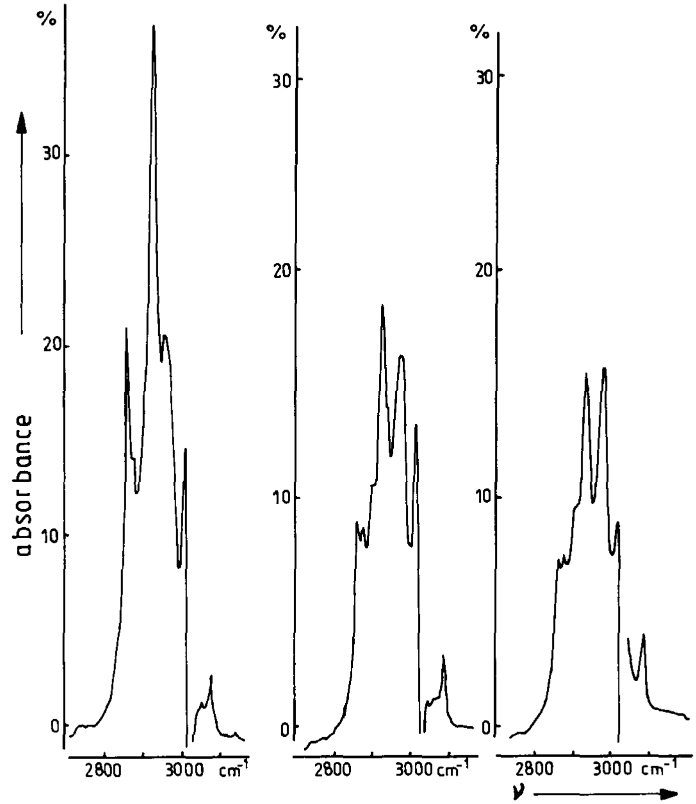


Fig. 2. (A) HPLC profiles of the hydrocarbons of the extract of the heat-pretreated brown coal (sample 1; a) and of a test mixture (b). Columns: Separon-SIX-NH_2 (150 × 3 mm I.D.) + Separon-SIX-CN (150 × 3 mm I.D.); 0.4 ml/min *n*-hexane; differential refractometer. (B) HPLC profiles of the hydrocarbons of the extract of the heat-pretreated brown coal (sample 1; a) and of a test mixture (b). Column: Separon-SIX-NH_2 (150 × 3 mm I.D.) + Separon-SIX-CN (150 × 3 mm I.D.); 0.4 ml/min *n*-hexane; UV detector 254 nm.

dominate in the NHC V fraction (mass numbers 39, 51, 65, 77, 91 and 105). In both fractions mass numbers 45, 59, 77 and 91 were found, suggesting the existence of ether groups in the compounds in these fractions, which has to be verified by other methods.



a) NHC I

b) NHC II

c) NHC V

Fig. 3. FT-IR spectra of the NHC fractions.

Detection of functional groups by HPLC of derivatives. The NHC of the NHC III and NHC IV fractions were derivatized with 2,4-dinitrophenylhydrazine [8] and 3,5-dinitrobenzoylchloride [9]. The derivatives of both reactions were separated by HPLC on a Vertex–LiChrosorb RP-18 column (250 × 4 mm I.D.) with a mixture of

TABLE II

SPECTRAL CHARACTERICS OF NHC

The aliphatic character of the compounds decreases with polarity.

Fraction	Hydrogen content (%)			
	H_{ar}	H_α	H_β	H_e
NHC I	1.70	3.80	67.87	26.60
NHC II	5.56	16.30	58.17	20.13
NHC III	9.20	27.30	49.02	16.20
NHC IV	12.00	22.76	45.82	19.43
NHC V	13.45	32.09	43.43	11.01

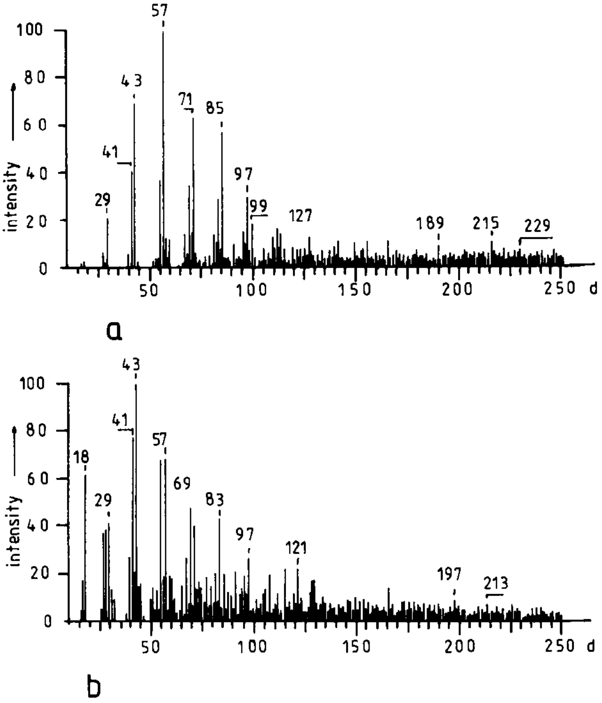


Fig. 4. Mass spectra of the NHC I (a) and NHC V (b) fractions.

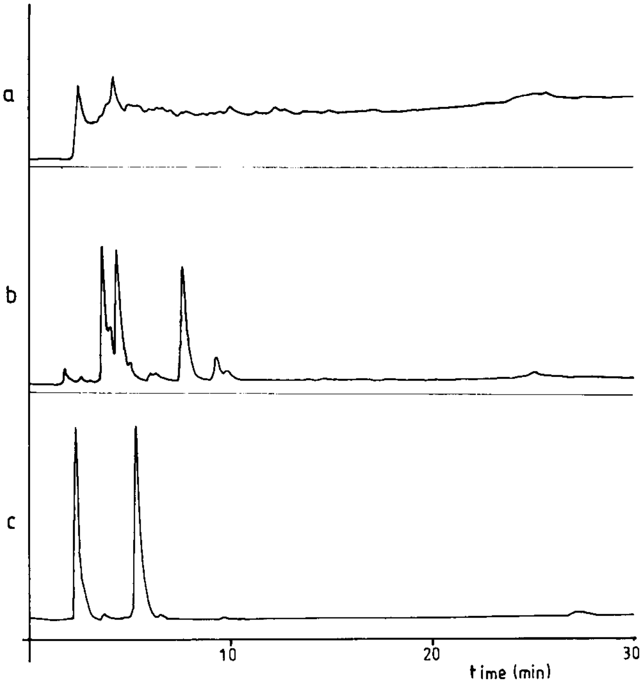


Fig. 5. HPLC profiles of the NHC III fraction (a), its 2,4-dinitrophenylhydrazones (b) and its 3,5-dinitrobenzoates. Column: LiChrosphere 100-RP-18 (5 μm; 250 × 4 mm I.D.). Elution: gradient from 75:25 methanol–water to 100% methanol in 20 min. Detection: UV filter photometer at 254 nm.

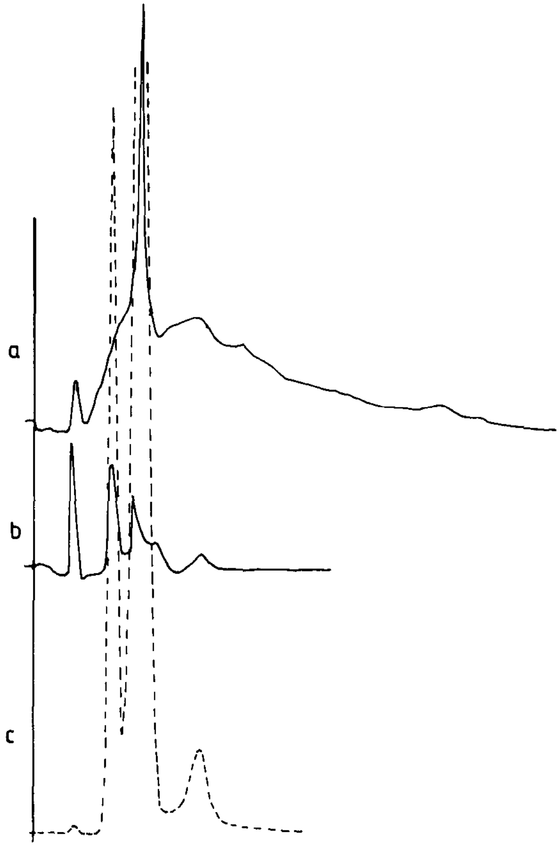


Fig. 6. HPLC profiles of the NHC IV fraction (a), its 3,5-dinitrobenzoates (b) and its 2,4-dinitrophenylhydrazones (c). Column: Vertex–LiChrosorb RP-18 (7 μm; 250 × 4 mm I.D.). Eluent: acetonitrile–water (60:40). Detection: UV filter photometer at 254 nm.

acetonitrile and water (60:40) or a gradient elution with methanol–water. The formation of 2,4-dinitrophenylhydrazones from C=O residues of the NHC III fraction is shown in Fig. 5. In Fig. 6 the formation of 2,4-dinitrophenylhydrazones from C=O residues and 3,5-dinitrobenzoates from OH residues in the NHC IV fraction is presented.

TABLE III

REACTION CONDITIONS AND YIELD OF HYDROCARBONS FROM TWO HYDROGENATION STEPS

	Step 1		Step 2
Amount of charge (g)	0.6		0.3
Reaction temperature (K)	653		698
Reaction time (min)	20		60
Catalyst		Fe^{II} sulphate	
Pressure of hydrogen at room temperature (MPa)	10		10
Yield of hydrocarbons (%)	32.1		32.4

Hydrogenation of the NHC

The NHC of sample 1 were carefully hydrogenated, taking special precautions to avoid side-effects of the mashing oil. The substances were first adsorbed on γ-aluminium oxide and were hydrogenated in two steps (Table III) in a 50-ml autoclave. The hydrocarbons formed in each step were separated by extrography, semipreparative and analytical HPLC (Figs. 7 and 8), and cGC. The structure-type composition found for each of the hydrogenation steps is listed in Tables IV and V.

It is evident that indanes, acenaphthenes, fluorenes and diphenyls were not formed in the second hydrogenation step. The unconverted NHC from both steps were characterized by ^{1}H-NMR (Fig. 9 and Table VI).

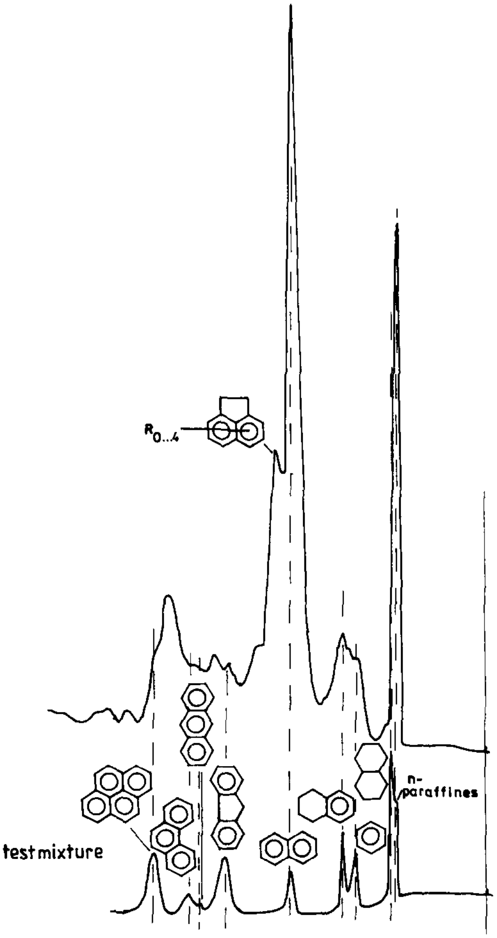


Fig. 7. Overview HPLC profile of the hydrocarbons of hydrogenation product 1 in comparison to a test mixture. For chromatographic conditions, see Fig. 2A.

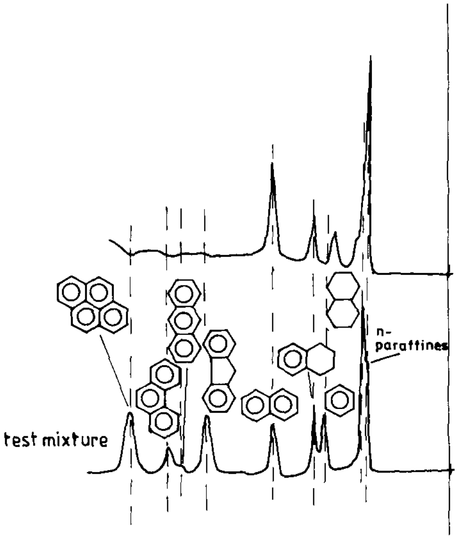


Fig. 8. Overview HPLC profile of the hydrocarbons of hydrogenation product 2 in comparison to a test mixture. For chromatographic conditions, see Fig. 2A.

TABLE IV

STRUCTURE-TYPE CHARACTERISTICS OF HYDROCARBONS IN THE PRODUCT OF THE HYDROGENATION STEP 1 (SEE ALSO FIG. 7)

Structure type	Content (%)	Qualitative composition
sCH	35.2	Paraffins > naphthenes
1 N-Ar	17.4	Alkylbenzenes, tetralenes/indanes
2 N-Ar	17.7	Naphthalenes, acenaphthenes, diphenyls, fluorenes
3 N+MN-Ar	24.4	Phenathrenes, pyrenes, chrysenes, polycyclic aromatics

TABLE V

STRUCTURE-TYPE CHARACTERISTICS OF HYDROCARBONS IN THE PRODUCT OF THE HYDROGENATION STEP 2 (SEE ALSO FIG. 8)

Structure type	Content (%)	Qualitative composition
sCH	28.6	Paraffins
1 N-Ar	18.7	Alkylbenzenes, tetralenes
2-N-Ar	27.1	Naphthalenes
3 N+MN-Ar	19.4	Polycyclic aromatics

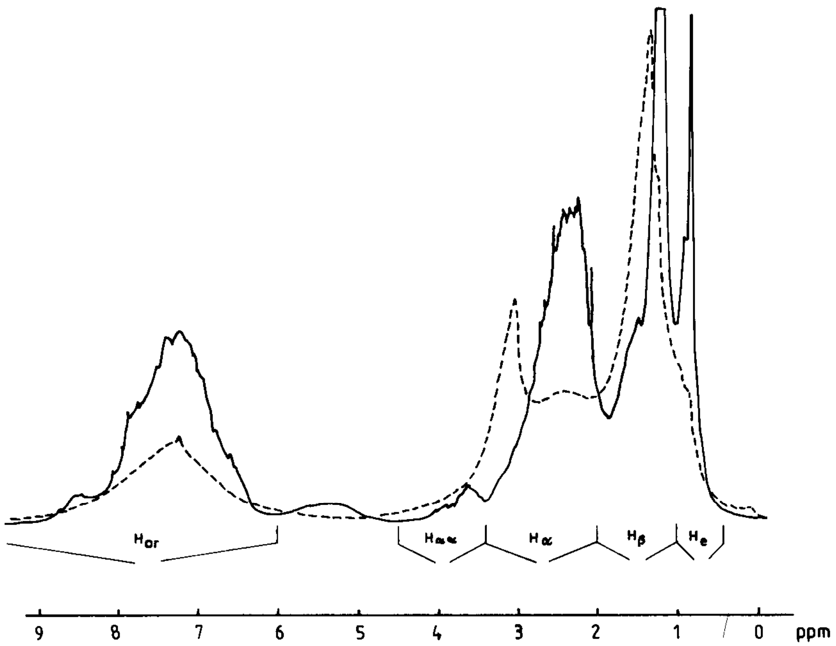


Fig. 9. ^{1}H-NMR spectra of NHC after (———) the first and (---) the second hydrogenation step.

TABLE VI

SPECTRAL CHARACTERISTICS OF NHC AFTER THE HYDROGENATION STEPS

Fraction	Hydrogen content (%)			
	H_{ar}	H_{α}	H_{β}	H_{e}
NHC before hydrogenation	9.44	22.04	51.12	17.40
NHC after step 1	26.05	28.73	33.42	10.13
NHC after step 2	14.17	34.90	50.97	–

CONCLUSIONS

Hydroxyl and carboxyl residues in NHC products of brown coal refining can be determined by derivatization and reversed-phase HPLC of the derivatives.

Circumstantial evidence for the existence of C–O–C residues can be deduced from the data of mass and FT-IR spectrometry.

The oxygen functional groups of NHC from brown coal refining products are bonded to aliphatic and naphthenic structures.

Heterocompounds containing aliphatic structures are preferentially hydrogenated to paraffins. Heterocompounds containing naphtheno-aromatic structures are hydrogenated by elimination of oxygen functional groups to aromatic and naphthenic hydrocarbons.

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