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Variations in the stable isotope ratios of specific aromatic and aliphatic hydrocarbons from coal conversion processes

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To establish the scope for applying gas chromatography–isotope ratio mass spectrometry (δ^{13}C GC–IRMS) to molecular recognition problems in coal utilisation, ^{13}C/^{12}C isotope ratios were determined for *n*-alkanes and polycyclic aromatic hydrocarbons (PAHs) as a function of coal rank and process conditions. Six coals ranging from a lignite to a low volatile bituminous coal were subjected to chloroform extraction, fixed-bed pyrolysis under hydrogen pressure (hydropyrolysis) and fluidised-bed (flash) pyrolysis. No significant variations in the stable isotope ratios of *n*-alkanes were evident as a function of either rank or conversion regime. In contrast, the isotope ratios of PAHs show large variations with those for hydropyrolysis (-23 to -25‰) being similar to the bulk values of the initial coals and being isotopically heavier (less negative) than their fluidised-bed pyrolysis counterparts by 2–3‰. However, the PAHs from fluidised-bed pyrolysis, which resemble closely those obtained from high temperature coal carbonisation, are still heavier (by 2–3‰) than those from diesel particulates and coal gasification and combustion residues. This provides a firm basis for the source apportionment of airborne PAHs in the proximity of coking plants, particularly with no major variations in the PAH isotope ratios being found as a function of rank.

Keywords: *Gas chromatography–isotope ratio mass spectrometry; coal; polycyclic aromatic hydrocarbons;* n-*alkanes; carbonisation; pyrolysis*

Compound-specific carbon isotope measurements became a practical reality with the development of reliable computer controlled gas chromatography–isotope ratio mass spectrometry (δ^{13}C GC–IRMS).[1,2] In this technique, a gas chromatograph is coupled to a combustion furnace and the isotopic composition of the resultant CO_2 (masses 45 for $^{13}CO_2$ and 44 for $^{12}CO_2$) is continuously analysed using a magnetic sector mass spectrometer. Similar isotopic compositions for a series of sedimentary compounds often imply that they have originated from the same biological source. Differences in isotopic composition of carbon-containing substances are expressed in terms of the conventional δ-notation giving the permil (‰) deviation of the isotope ratio of a sample (sa) relative to that of a standard (st), *i.e.*,

$$\delta^{13}\mathrm{C}_{\mathrm{sa}} = \left[\frac{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{sa}}}{(^{13}\mathrm{C}/^{12}\mathrm{C})_{\mathrm{st}}} - 1\right] \times 10^{3} \qquad (‰, \mathrm{PDB})$$

The standard commonly used is Peedee belemnite (PDB), a Cretaceous marine carbonate sample, whose δ^{13}C value defines 0‰ on the δ-scale.

The potential of compound-specific isotopic analysis for source apportionment of polycyclic aromatic hydrocarbons (PAHs) in environmental samples has been demonstrated recently by O'Malley and co-workers[3,4] and the present authors.[5] Analysis of sediments taken from St. John's Harbour and Conception Bay (Newfoundland) by O'Malley *et al.*[3] indicated that PAHs arising from wood burning and vehicle emissions exhibited significantly different isotopic signatures. Furthermore, the isotopic compositions of *n*-alkanes and PAHs produced from combustion of C_3 and C_4 plant species were reported.[4] We found that the ^{13}C/^{12}C isotopic ratios for PAHs derived from coal and wood pyrolysis and diesel particulates vary over a range of about 8‰, which should readily provide a basis for source apportionment in a number of environments.[5]

Although δ^{13}C GC–IRMS has been widely used in a large number of petroleum geochemical studies,[6] apart from our own exploratory investigation of PAHs[5] the technique has only been applied to coal derivatives by one other group thus far.[7] However, the study was confined to only low-yield solvent extracts from a bituminous and a low-rank coal with the δ^{13}C values for the aliphatic and aromatic species reported being consistent with a higher plant origin. Stable carbon isotopic analysis of whole oils, source rocks and bulk hydrocarbon fractions is an extremely well established technique in the petroleum industry to aid source rock–oil correlations,[8] and this more traditional approach has also been used to identify the contributions from coal and oil to different product fractions in coprocessing coal and oil in hydroliquefaction[9]

Before δ^{13}C GC–IRMS can properly be applied to molecular problems in coal utilisation, such as sourcing PAH emissions, a comprehensive understanding is needed of how stable isotope ratios vary for hydrocarbons derived from coal. This paper reports the isotopic variations that occur for *n*-alkanes and PAHs as a function of coal rank and process conditions. Six coals ranging from a lignite to a low volatile bituminous coal were subjected to simple chloroform extraction, pyrolysis under hydrogen pressure (hydropyrolysis) and fluidised-bed (flash) pyrolysis and the resultant tars and extracts were fractionated to yield aliphatic and aromatic fractions for GC–IRMS analysis. In addition, the results obtained were compared with those reported elsewhere for PAHs in particulates obtained from gasification and from fluidised-bed combustion[10] to help establish a firm basis for the source apportionment of PAHs in the proximity of coking plants.

Experimental

Sample selection

A suite of six coals taken from the British Coal Sample Bank (Table 1) ranging in rank from a lignite (Hambach, Germany; mean random reflectance, R_0, of 0.28) to a low volatile bituminous coal (Cwm, R_0 = 1.37) were selected for investigation . The coals were subjected to (i) solvent extraction with chloroform (under reflux for 10 h), (ii) fixed-bed hydropyrolysis at 650 °C and (iii) fluidised-bed pyrolysis at 900 °C.

Details on the procedures used for fluidised-bed pyrolysis[11,12] and hydropyrolysis[13,14] have been reported elsewhere. In order to obtain aromatic fractions in high yield where the parent PAHs are dominant, the hydropyrolysis tests were carried out at a relatively high temperature of 650 °C with a pressure of 15 MPa. For the same reason, the fluidised-bed pyrolysis tests were conducted at 900 °C, which yields PAH fractions very similar to those obtained from high temperature carbonisation used to produce blast furnace coke.

After solvent removal, the hydropyrolysis and fluidised bed pyrolysis tars and the chloroform extracts were fractionated by open column alumina chromatography (fine grain activated neutral alumina; Brockmann Grade I) to yield aliphatic and aromatic fractions for δ^{13}C GC–IRMS analysis. Hexane (HPLC grade) was used to elute the aliphatics with subsequent elution of the aromatics in toluene (analytical-reagent grade). In addition, to examine the ring number distributions for the aromatic fractions obtained from fluidised-bed pyrolysis and hydropyrolysis, HPLC analysis was carried out.

Gas chromatography–isotope ratio mass spectrometry

The compound-specific δ^{13}C measurements were carried out on the aliphatic and aromatic fractions using a VG (Winsford, Cheshire, UK) Isochrom II GC–IRMS instrument. Initial separation of the components was obtained on a WCOT 25 m fused silica capillary column coated with CP Sil 5CB. Samples were injected in the split mode (splitting ratio 30 : 1) and helium was employed as the carrier gas with a temperature programme from 50 °C (held for 3 min) at 5 °C min^{-1} to 300 °C (held for 15 min) being employed. The injection and detection temperatures were both set at 320 °C. As components were eluted from the column they were passed, in a stream of helium, into a CuO oxidation furnace at 850 °C where all of the organic compounds were converted into CO_2 and water. The water was then removed by means of a cryogenic trap, cooled by liquid nitrogen and heated to −100 °C, and the CO_2 was continuously measured by a stable isotope mass spectrometer. All component peaks were identified by comparison of retention times with EPA standards (Supelco, Bellefonte, PA, USA). Reported isotopic data represent the arithmetic means of at least two duplicate analyses and the estimated repeatability for individual hydrocarbons, based on an earlier study with the VG Isochrom II GC–IRMS system,[15] was 0.2–0.4%. The experimental error of the instrument was betweeen 0.5 and 1.0‰, with the precision decreasing as the intensity of the GC peaks decreased in relation to the unresolved background. The complexity of the GC traces for the chlorofrom extract aromatics meant that the unresolved background was too great to facilitate reliable compound-specific δ^{13}C measurements.

The carbon stable isotope ratios of the coal samples (Table 3) were determined by conventional sealed-tube combustion to precisions better than 0.1%.

High-performance liquid chromatography

For HPLC separation of the aromatic fractions by ring size, a proprietary electron deficient, nitroaromatic-bonded silica column manufactured by Shandon (London, UK) (Hypersil CTA normal-phase column, 25 cm × 4.6 mm id, 5 μm particles) was used in conjunction with an Applied Chromatography Systems (Macclesfield, UK) Model 352 gradient elution pump, a Waters (Milford, MA, USA) Model 486 UV detector at 254 nm and a PC-based software package for peak integration. The volumetric flow rate was set at 0.6 cm^3 min^{-1} and a standard mixture of 16 PAHs was used to optimise the separation achieved with hexane and dichloromethane (DCM) mixtures, the most satisfactory gradient elution scheme being 10% v/v DCM in hexane for 20 min, then from 10 to 100% v/v DCM during 60 min and, finally, 100% v/v DCM.

Results and discussion

Yields

The yields of aromatic and aliphatic fractions from fluidised-bed pyrolysis, hydropyrolysis and chloroform extraction of the coals are given in Table 2. As expected, chloroform extraction gives extremely low yields of GC-amenable aliphatics and aromatics. The yields of tar and aromatic material from fluidised-bed pyrolysis and hydropyrolysis decrease with increasing rank but, owing to the use of a high hydrogen pressure, the yields are much greater from hydropyrolysis with the differences in yield becoming more apparent with increasing rank. Hence, on the basis of yield alone, the aromatics obtained from hydropyrolysis are expected to be more representative of the parent coals than those from fluidised-bed pyrolysis.

n-*Alkanes*

Fig. 1 summarises the stable isotope ratios for the *n*-alkanes obtained from the chloroform extracts and shows that there is no systematic variation in the δ^{13}C values as a function of rank and conversion regime, with values occurring in the range −27 to −30‰. The only possible exception is Hambach lignite, where the values decreased slightly with increasing carbon number, possibly owing to the increasing influence of higher plant material that has a lower stable isotope ratio than alginite,[16] which accounts for 10% of the organic matter in this lignite. The δ^{13}C values for the *n*-alkanes in the fluidised-bed pyrolysis and hydropyrolysis tars from all the coals investigated are summarised in Table 3. Again, no significant variations are evident, indicating that neither rank nor the mode of conversion affects the δ^{13}C values. The *n*-alkanes are isotopically lighter than the whole coals whose stable isotope ratios occur over a relatively narrow range (Table 3), confirming that long *n*-alkyl chains from higher plants represent only a minor input into coal deposits.

Table 1 Properties of coals selected for investigation

	Proximate analysis (% as received)					Ultimate analysis (% dry mineral matter free)			
Sample	Vitrinite reflectance	Moisture	Ash	Volatile matter	Fixed carbon	C	H	O	N
Hambach	0.28	18.0	3.5	41.0	37.5	67.5	4.4	27.2	0.03
Nadins	0.44	13.3	7.4	34.9	44.4	80.1	5.1	12.0	1.9
Gedling	0.54	10.0	2.0	34.5	53.5	81.6	5.2	10.3	1.7
Point of Ayr	0.85	2.4	9.8	32.7	55.1	87.2	5.8	4.6	1.6
Cwm Bargoed	1.06	1.0	2.8	28.5	67.7	88.5	4.9	4.2	1.6
Cwm	1.37	0.7	5.9	20.9	72.5	90.3	4.4	3.0	1.5

Polycyclic aromatic hydrocarbons

Gas chromatograms of the aromatic fractions obtained from hydropyrolysis and fluidised bed pyrolysis of Cwm coal are presented in Fig. 2, which shows that the parent PAHs are prominent for both types of tar. Table 3 summarises the carbon stable isotope ratios found for the PAHs in the fluidised-bed and hydropyrolysis tars and Fig. 3 shows the variations in the $\delta^{13}C$ values for the 16 US Government EPA-listed PAHs for the fluidised-bed tars. In contrast to the *n*-alkanes, the carbon stable isotope ratios of the PAHs show major and consistent variations with processing conditions. Those from hydropyrolysis (−23 to −25‰) are isotopically heavier (less negative) than their counterparts from fluidised-bed pyrolysis, typically by about 2–3‰ (Table 3 and Fig. 3). No major variations in the PAHs isotope ratios are evident with increasing coal rank (Table 3). Indeed, the $\delta^{13}C$ values for the hydropyrolysis PAHs resemble those of the parent coals (Tables 1 and 3). Despite the relatively high process severity, hydropyrolysis is known to preserve a number of structural features of coals and petroleum source rocks.[14,17] Thus, the aromatics released by hydropyrolysis are considered as being reasonably representative of the aromatic moieties in the parent coals in terms of not being subjected to hydrocracking and condensation reactions to an extent that may cause isotopic fractionation. To highlight the effect of processing conditions on product isotopic composition, Fig. 4 compares the stable carbon isotope ratios of the PAHs and *n*-alkanes obtained from the hydropyrolysis, fluidised-bed pyrolysis and chloroform extraction of Gedling coal.

The HPLC-determined aromatic ring size distributions for the aromatics obtained from each of the coals under the fluidised-bed and hydropyrolysis regimes are summarised in Table 4. Fig. 5 shows the HPLC traces obtained for the aromatics from the hydropyrolysis and fluidised-bed pyrolysis tars for Cwm coal. In all cases, the majority of the aromatics

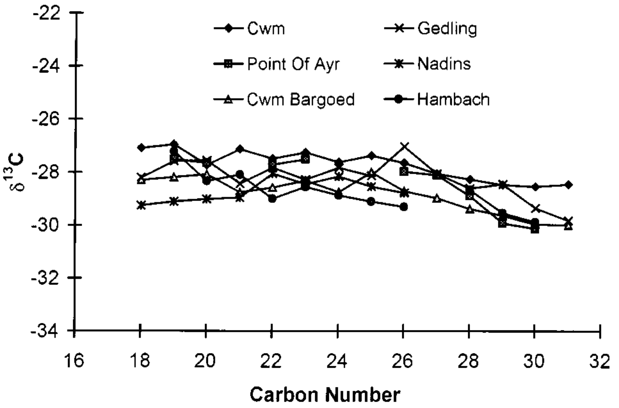

Fig. 1 Variation in the *n*-alkane carbon stable isotope ratios for the aliphatics from chlorofrom extraction of the coals investigated.

Table 2 Yields of total tar/extract, aliphatics and aromatics obtained from chloroform extraction, hydropyrolysis and fluidised bed pyrolysis of the coals investivated

	Fluidised bed pyrolysis (% dry ash-free basis coal)			Hydropyrolisis (% dry ash-free basis coal)			Chloroform extraction (% dry ash-free basis coal)	
Sample	Tar	Aromatics	Aliphatics	Tar	Aromatics	Aliphatics	Aliphatics	Aromatics
Hambach	38	18	3	51	31	3	0.09	0.15
Nadins	28	13	2	43	22	4	0.14	0.09
Gedling	27	14	2	35	21	2	0.12	0.24
Point of Ayr	25	12	3	35	21	4	0.11	0.26
Cwn Bargoed	18	11	1	27	19	3	0.05	0.16
Cwm	15	8	3	25	18	3	0.02	0.05

Table 3 Summary of the carbon stable isotope ranges for the whole coals and the *n*-alkanes and PAHs from chloroform extraction, hydropyrolysis (HyPy) and fluidised-bed pyrolysis (FBP)

Coal (bulk value, ‰)	Carbon content (%)	Vitrinite reflectance	Chloroform aliphatics (‰)	HyPy aliphatics (‰)	HyPy aromatics, 2–3 ring (‰)	HyPy aromatics, 4 ring (‰)	HyPy aromatics, 5–6 ring (‰)	FBP aliphatics (‰)	FBP aromatics, 2–3 ring (‰)	FBP aromatics, 4 ring (‰)	FPB aromatics, 5–6 ring (‰)
Hambach (−25.6)	67.5	0.28	−27.2 to −29.9	−27.5 to −29.5	−25.2 to −25.7	−25.4 to −26.0	−25.1 to −25.6	−27.8 to −30.1	−28.5 to −28.6	−26.6 to −28.0	−26.4 to −27.8
Nadins (−23.8)	80.1	0.44	−28.1 to −31.7	−28.9 to −29.7	−23.2 to −23.9	−23.1 to −24.1	−23.2 to −24.3	−27.8 to −29.3	−27.2	−26.6 to −27.2	−27.3 to −28.0
Gedling (−23.8)	81.6	0.54	−27.6 to −29.8	−29.3 to −30.0	−23.6 to −24.0	−23.9 to −24.2	−24.0 to −24.7	−27.9 to −30.0	−24.5 to −25.2	−26.4 to −27.2	−26.1 to −29.4
Point of Ayr (−23.0)	87.2	0.85	−27.5 to −30.1	−27.3 to −30.7	−23.5 to −24.1	−23.3 to −23.8	−23.5 to −24.8	−29.1 to −30.6	−25.5 to −26.8	−26.7 to −28.2	−27.3 to −28.9
Cwm Bargoed (−23.9)	88.5	1.06	−28.0 to −30.0	−28.6 to −31.0	−23.3	−23.0 to −23.7	−23.2 to −25.0	−28.1 to −29.9	−25.8	−26.0 to −26.9	−27.0 to −27.9
Cwm (−23.7)	90.3	1.37	−27.0 to −28.6	−29.1 to −29.7	−24.1	−23.5 to −24.5	−24.0 to −25.3	−28.0 to −30.2	−25.6 to −27.6	−25.0 to −27.2	−27.5 to −27.9

occur in the 2–3 ring range for hydropyrolysis, whereas fluidised-bed pyrolysis gives rise to significantly more 4–6 ring PAHs. The gas chromatograms for the Cwm coal aromatic fractions also reveal the same trend (Fig. 2). The smaller average ring size for the hydropyrolysis PAHs provides further evidence that they are more representative of the aromatic moieties in the parent coals than their fluidised-bed counterparts.

The $\delta^{13}C$ values of the PAHs from fluidised-bed pyrolysis generally decrease slightly (become lighter) with increasing ring size (Fig. 3). The average value for phenanthrene and anthracene is about −27‰ compared with about −28‰ for benzo[*a*]pyrene and dibenz[*a*,*h*]anthracene (Fig. 3). Although the PAHs from fluidised-bed pyrolysis are isotopically lighter than their hydropyrolysis counterparts and the parent coals, they are still isotopically heavier by about 2–3‰ than those obtained

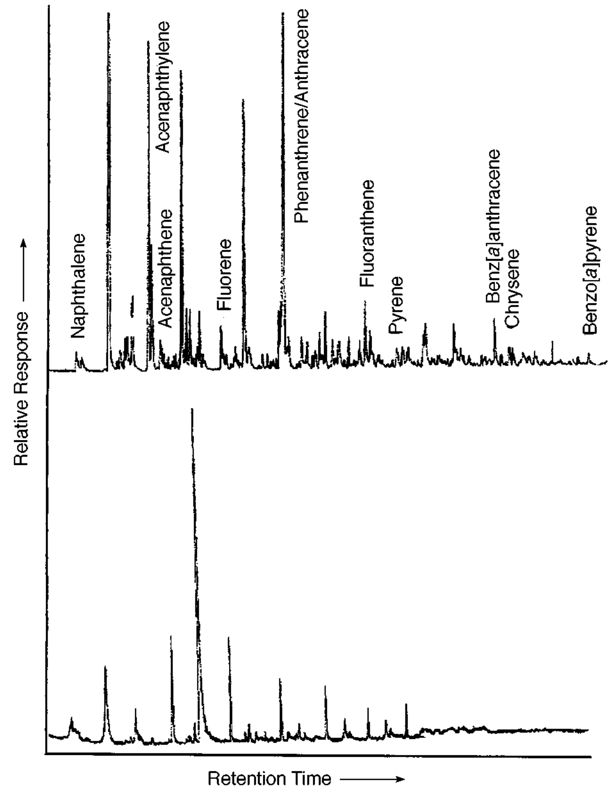

Fig. 2 Gas chromatograms of the aromatics from the fluidised-bed pyrolysis (top) andhydropyrolysis (bottom) tars for Cwm coal.

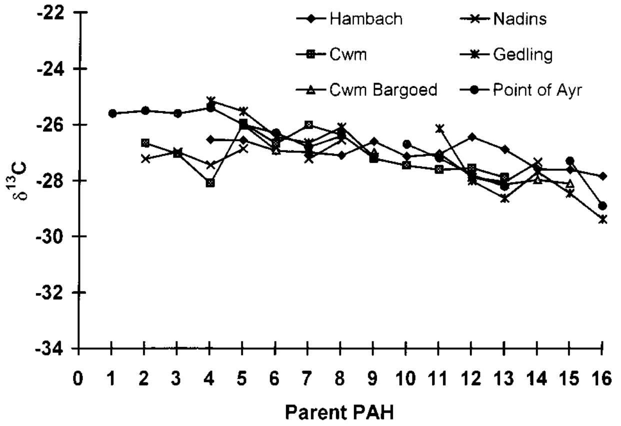

Fig. 3 Variation in the carbon stable isotope ratios for the PAHs from fluidised-bed pyrolysis at 900 °C of the coals investigated. 1, Naphthalene; 2, acenaphthylene; 3, acenaphthene; 4, fluorene; 5, phenanthrene; 6, anthracene; 7, fluoranthene; 8, pyrene; 9, benz[*a*]anthracene, 10, chrysene; 11, benzo[*b*]fluoranthene; 12, benzo[*k*]fluoranthene; 13, benzo[*a*]pyrene; 14, dibenz[*a*,*h*]anthracene; 15, benzo[*ghi*]perylene; 16, indeno[123-*cd*]pyrene.

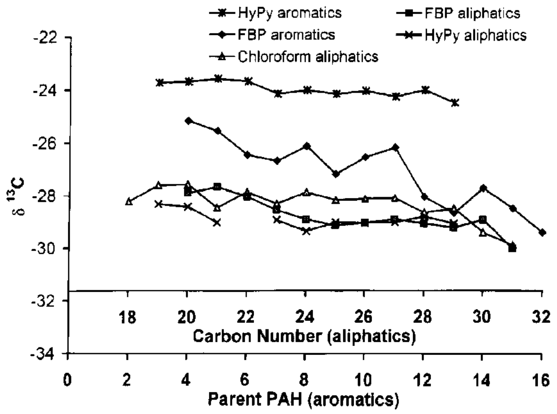

Fig. 4 Variation in the carbon stable isotope ratios of the *n*-alkanes and PAHs obtained from the hydropyrolysis, fluidised bed pyrolysis and chloroform extraction of Gedling coal.

Table 4 HPLC-determined distributions of PAHs according to ring size in the aromatics from fluidized bed pyrolysis (FBP) and hydropyrolysis (HyPy) of coals (normalised to 100%)

	2–3 ring (%)		4 ring (%)		5–6 ring (%)	
Sample	FBP	HyPy	FBP	HyPy	FBP	HyPy
Hambach	78	84	17	16	5	< 1
Nadins	66	80	26	19	8	1
Gedling	71	78	15	20	13	2
Point of Ayr	75	81	15	17	10	2
Cwm Bargoed	71	73	18	16	11	3
Cwm	87	88	5	12	8	1

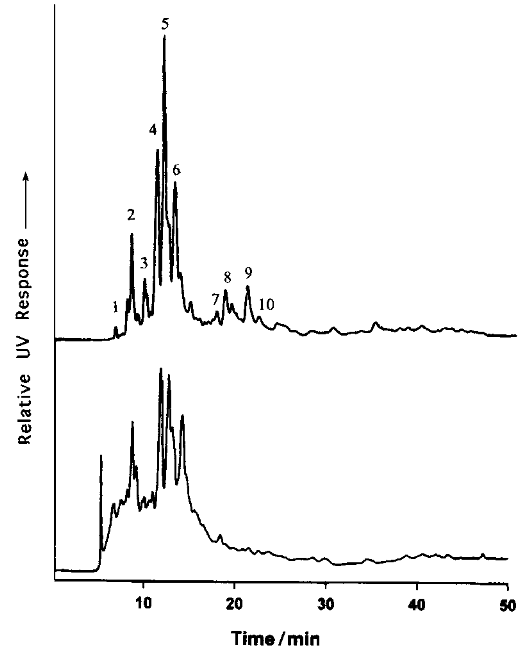

Fig. 5 HPLC traces for the aromatics obtained from the fluidised-bed pyrolysis (top) and hydropyrolysis (bottom) tars for Cwm coal.1, Naphthalene; 2, fluorene; 3, acenaphthene; 4, acenaphthylene; 5, anthracene; 6, phenanthrene; 7, fluoranthene; 8, benz[*a*]anthracen;, 9, pyrene; 10, chrysene.

from both fluidised-bed combustion and gasification of coal (values of −28 to −31‰ reported elswhere for a series of particulates[10]). These differences in the stable isotope ratios of coal-derived PAHs can be rationalised in general terms by the ring condensation that occurs during high temperature devolatilisation. For larger PAHs to form, the smaller ones in the primary volatiles must undergo a series of complex transformations involving carbon–carbon bond formation, cyclisation and/or ring fusion. In one or all of these processes, ^{12}C may be preferentially incorporated into the PAHs where a kinetic isotope effect is operative, leading to a depletion of the heavy ^{13}C isotope in higher molecular mass species. Hence, PAHs from coal combustion and gasification may have undergone more ring condensation than those formed in fluidised-bed pyrolysis.

Sourcing PAH in the environment

The results have demonstrated that the PAHs from high temperature pyrolysis, which should correspond fairly closely to those obtained from coal carbonisation plants, are isotopically lighter than the parent coals, but they are still considerably heavier (by 2–3‰) than those obtained in particulates from the combustion of a typical UK diesel blend,[5] combustion and gasification of coals (−28 to −31‰).[10] Furthermore, since no major variations exist in the PAH isotopic ratios, the results obtained provide a firm basis for sourcing PAHs unequivocally from coking plants and resolving diesel-particulate contributions in urban environments. Indeed, our continuing research effort includes the analysis of a wide selection of airborne particulates and dust samples in the proximity of carbonisation plants in the UK.

Conclusions

No significant variations exist in the stable isotope ratios of *n*-alkanes derived from coal as a function of either rank or conversion regime.

The stable isotope ratios of coal-derived PAHs show large variations. Those for PAHs obtained in relatively high yield by hydropyrolysis (−23 to −25‰) are similar to the bulk values of the initial coals. PAHs from fluidised-bed pyrolysis are lighter (more negative) by 2–3‰ than their counterparts from hydropyrolysis, but are still heavier (again by 2–3‰) than those from coal gasification and combustion residues

The PAHs from fluidised-bed pyrolysis, which closely resemble those obtained from high temperature coal carbonisation, are still isotopically heavier (by 2–3‰) than those from diesel particulates and coal gasification and combustion residues. This provides a firm basis for the source apportionment of airborne PAHs in the proximity of coking plants, particularly with no major variations in the PAH isotope ratios being found as a function of rank.

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