

THE USE OF PHENOLIC RESINS CONTAINING POLYNUCLEAR AROMATIC MOIETIES TO MODEL ASPECTS OF COAL PYROLYSIS

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Keywords: Phenolic resins, polycyclic aromatic hydrocarbons, carbonisation

INTRODUCTION

Coals and oil shales have highly complex, macromolecular organic structures¹⁻³ and, in order to obtain insights into the multitude of reactions which occur during their thermal breakdown, detailed compositional information on the aromatic, aliphatic and heteroatomic groups present and an understanding of how these different functionalities behave under processing conditions are required. To achieve the latter goal, model compound studies performed in both vapour and liquid phases have been used extensively⁴. However, a major drawback with such studies is that radical species generated by bond homolysis are mobile and free to diffuse independently prior to further reaction. In contrast, for highly cross-linked macromolecular solids such as coals and oil shales, many of the reactive intermediates remain covalently attached to the matrix of the solid and thus their reactivity is subject to diffusional constraints. Further, for thermal studies in open systems the use of non-softening substrates that neither melt nor vaporise and hence remain in the reactor is essential.

In order to probe the effects of restricted mobility in free radical reaction pathways during coal liquefaction, Buchanan and co-workers studied the thermal decomposition of model compounds immobilised on silica^{5,6}. It was recognised that these substrates also have considerable potential for modelling many aspects of solid fuel behaviour, including the release of sulphur and nitrogen species during coal conversion processes and the cleavage of diphenylalkane bridging groups during pyrolysis. Preliminary work establish that the SiO-C bond linking the substrate to the surface is reasonably stable and does not cleave below 500°C⁷. Immobilised sulphur moieties, typical of those found in solid fuels were subsequently prepared and used as calibrants in temperature programmed reduction (TPR)⁸, a thermal technique used to specify organic sulphur forms from their characteristic reduction temperatures^{9,10}.

Cured phenol-formaldehyde (PF) resins were identified as another flexible class of materials that could be used for investigating thermochemical phenomena in the solid state since a wide spectrum of hydrocarbon and heteroatomic moieties can readily be introduced into their macromolecular framework. A series of sulphur and nitrogen containing co-resoles and resites have been prepared and their characterisation has been reported previously¹¹. These resites have been used to study the release of sulphur dioxide during coal combustion¹² and as an alternative calibrant to the silica immobilised substrates for TPR^{13,14}.

Polycyclic aromatic hydrocarbons (PAH) are a series of ubiquitous environmental pollutants containing two or more fused benzene rings that are widely produced by the incomplete combustion of fossil fuels and other organic materials¹⁵⁻¹⁷. Due to the lack of mechanistic information concerning their formation during solid fuel conversion processes, there is a need for suitable model substrates and, in this investigation, a suite of PAH-containing resites have been prepared, with, as the second component, diphenylmethane, benzylanthracene, benzylphenanthrene, benzylphenanthrene and 2-naphthol. To illustrate the potential of the resites to study the formation of PAH in the utilisation of solid fuels, the carbonisation of the 9-(4-hydroxybenzyl)anthracene-containing resite has been investigated in a fluidised-bed reactor.

EXPERIMENTAL

Synthesis of precursors

The mono- or dihydroxydiphenylalkane and monohydroxy-phenyl PAHs used to prepare the resins were 4-hydroxy-diphenylmethane, 4,4'-dihydroxydiphenylethane, 2-naphthol, 4-naphthobenzylphenol, 9-(4-hydroxybenzyl)anthracene and 9-(4-hydroxybenzyl)phenanthrene. Of these, only 4-hydroxydiphenylmethane and 2-naphthol were commercially available.

To prepare 4,4'-dihydroxydiphenylethane, a Wolff-Kishner reduction was conducted on 4'-methoxy-2-(p-methoxyphenyl)acetophenone (deoxyanisoin) to yield 4,4'-

dimethoxydiphenylethane. This compound was then subjected to demethylation by refluxing for 20 minutes in 20 g of redistilled pyridine hydrochloride. This yielded the crude product which was recrystallised from hexane-ethylacetate to yield white shiny prismatic crystallites (M.Pt. 198-199°C).

To prepare 1-(4-hydroxybenzyl)naphthalene, naphthalene was first acylated with p-anisoylchloride to yield 1-(4-methoxybenzoyl)naphthalene. A Wolff-Kishner reduction was conducted on this compound to produce 1-(4-methoxybenzyl)naphthalene. This compound was then demethylated as described above. After cooling, the reaction product was extracted in diethylether and purified by vacuum distillation (180-182°C, 3-4 mmHg). The product was recrystallised from benzene-acetone (3:1 v/v) to yield yellow shiny needle crystallites (M.Pt. 166-167°C).

9-(4-hydroxybenzyl)anthracene was prepared by first reacting 9-anthracenecarboxylic acid with oxalylchloride to yield 9-anthracene carbonyl chloride. This was then acylated with anisole to produce 9-(4-methoxybenzoyl)anthracene which was then subjected to a Wolff-Kishner reduction. The resultant 9-(4-methoxybenzyl)anthracene was then demethylated as described above and the crude product was recrystallised from toluene to yield yellow shiny needle crystallites (M.Pt. 187-188°C).

To prepare 9-(4-hydroxybenzyl)phenanthrene, phenanthrene was first acylated with p-anisoylchloride to yield 9-(4-methoxybenzoyl)phenanthrene. A Wolff-Kishner reduction was conducted on this compound to yield 9-(4-methoxybenzyl)phenanthrene which was then demethylated as described earlier. The crude product was purified by vacuum distillation (200-201°C, 3-4 mmHg) and recrystallisation from hexane which yielded yellow shiny needle crystallites (M.Pt. 85-86°C).

Synthesis of resins

The co-resoles were prepared using a total phenol to formaldehyde mole ratio of 1:2.5 following established procedures^{18,19}. The mole ratio of phenol to the monohydroxydiphenylalkanes or monohydroxybenzyl PAHs was 3:1 to ensure that a reasonably high degree of crosslinking was achieved in the initial resoles. Sodium hydroxide was used as catalyst in the condensation reaction with mole ratio of 0.1 with respect to phenol. Phenol, the monohydroxydiphenylalkane or monohydroxybenzyl PAHs and formaldehyde (37% formaldehyde) were mixed in 250 cm³ 3-neck round bottom flask and stirred until all the phenol was in solution. The mixture was then cooled in an ice-bath for about 10 minutes before sodium hydroxide (0.006 mol, 20 M) was added dropwise to the reaction mixture. This was then refluxed at 70°C for 30 min., acidified with 85% lactic acid to a pH of 4-5 (indicated by universal indicator paper) before excess water was removed by vacuum distillation. The thick resinous material was poured into a capped container for curing in an oven purged with nitrogen gas that was initially set at 70°C for 4 days. The oven temperature was then raised to 130 and 200°C for additional 24 hour periods. For purposes of comparison, a normal PF resite and resole were prepared by the same procedure.

Pyrolysis

An all-silica fluidised-bed reactor system (5 cm dia.), based on the design used by Tyler and coworkers²⁰, was used to pyrolyse a normal PF resite and the 9-(4-hydroxybenzyl)anthracene - containing resite at a temperature of 900°C in a bed containing ca. 100g of acid-washed sand (200-300 μ). This was fluidised using a flow of 2-3 dm³ min⁻¹ of nitrogen. Approximately 4 g of resite (75-212 μ) was fed at a constant rate from a hopper, which was also fluidised with a flow of nitrogen (1 dm³ min⁻¹), over 20-30 minute period into the fluidised-bed at 900°C. Two 500 cm³ Dreschel bottles in series cooled with dry ice were used to trap the tars with virtually no carry over into the gas.

After the tests, the tars were recovered in toluene for analysis. The char and tar yield were calculated from the weight gains of the bed and the traps during each run with the weight gains of the traps being corrected for any water present determined via the Dean-Stark method. After the water had been removed from the toluene solutions of the tars, these were concentrated to facilitate fractionation of the tars by preparative-scale open-column alumina chromatography to provide aromatic fractions for high performance liquid chromatography (HPLC) analysis. The alkanes, aromatics and polars were eluted successively from the column containing activated alumina (500°C for 16 hr.) with n-hexane, toluene and methanol.

For HPLC separation of the aromatic fractions by ring size, an electron-deficient, nitroaromatic-bonded silica column manufactured by Shandon (Hypersil CTA) was used in conjunction with an

Applied Chromatography Systems gradient elution pump, a Waters UV detector at 254 nm and a PC-based software package for peak integration. The volumetric flowrate was set at $0.6 \text{ cm}^3 \text{ min}^{-1}$ and a standard mixture of 16 PAHs (supplied by Supelco) was used to optimise the separation achieved with n-hexane and dichloromethane (DCM) mixtures, the most satisfactory gradient elution scheme being 10 % v/v DCM in hexane for 20 min., followed by 10 to 100 % v/v DCM in 60 min. and, finally, 100 % v/v DCM.

RESULTS AND DISCUSSION

The total yields of tar and aromatics and the yield of anthracene obtained from the fluidised-bed pyrolysis experiments on the normal PF and the 9-(4-hydroxybenzyl)anthracene-containing resite are listed in Table 1, together with the HPLC-determined distribution of ring size in the aromatics. Figure 1 compares the HPLC traces for the aromatics obtained from the two resites. The high pyrolysis temperature of 900°C ensures that parent PAH dominate over the alkyl-substituted counterparts (most alkyl and parent PAH co-elute in the HPLC separation). As expected from the volatile matter contents also shown in Table 1, a much higher tar yield has been obtained from the 9-(4-hydroxybenzyl)anthracene-containing resite. Indeed, the higher tar yield is accounted for completely by the additional aromatic material obtained (*ca.* 10% w/w resite).

As anticipated, anthracene dominates the HPLC trace of the aromatics for the 9-(4-hydroxybenzyl)anthracene-containing resite (Figure 1, phenanthrene being the major peak in the trace for the normal resite). However, the increase in anthracene yield of *ca.* 5% w/w resite only accounts for about half that in the total tar yield. Further, when this fact is taken with the estimated anthracene content of *ca.* 30% in the initial resite, strong evidence emerges for the anthracene becoming involved in many other reaction pathways other than simple homolytic cleavage of the anthracylbenzyl methane linkage. Since the total tar yield is only 34%, it can be inferred that a substantial portion of the anthracene is incorporated into the char. Further, the following HPLC results provide evidence that some of the anthracene present rearranges to form other low molecular mass PAH, particularly phenanthrene and acenaphthene, during pyrolysis.

Table 2 compares the mass ratios of phenanthrene (the major constituent in the aromatics from the normal resite, Figure 1) to a number of other PAH present. With the exception of acenaphthene, the ratios increase considerably indicating that the yields of phenanthrene and acenaphthene are both considerably greater for the 9-(4-hydroxybenzyl)anthracene-containing resite with the implication that they have been formed by rearrangement of the anthracene present. Indeed, it is estimated from the data in Table 2 that the phenanthrene yield increases from 2.2% (w/w) for the normal resite to 5.5% for the 9-(4-hydroxybenzyl)anthracene-containing resite.

The fact that the yield of aromatic material is significant from the normal PF resites provides direct evidence that phenolic moieties can transform directly into PAH during devolatilisation. The first step in this complex reaction pathway probably involves dehydration to form diphenyl ether and furan moieties, which then undergo subsequent ring growth with further dehydration. Since phenolic moieties are the major building blocks of both low-rank and high volatile bituminous coals¹, these are likely to be the prime source of PAH rather than the much smaller concentrations of large aromatic ring systems in these coals.

CONCLUSIONS

Although van Krevelen was the first to use PF resins in coal science to account for the plasticity behaviour of different coals¹, the approach adopted here for PAH represents a new direction in fuel science for investigating, in a macromolecular environment, the behaviour of the individual functional groups present during conversion processes. Non-softening PF co-resites are ideal substrates for probing the reaction pathways leading to PAH formation during devolatilisation since they facilitate the incorporation of individual PAHs into a highly cross-linked matrix. The volatile matter contents of the PAH-containing resites were higher than the corresponding normal PF resins due to the lability of the single diarylmethane linkage anchoring the PAHs into the macromolecular structure. The carbonisation of the normal PF and 9-(4-hydroxybenzyl)anthracene-containing resite in a fluidised-bed reactor served to illustrate the complexity of the reaction pathways undergone by the anthracene moiety, with evidence of rearrangement of the anthracene structure to form other PAH, primarily phenanthrene and acenaphthene.

REFERENCES

1. W. Van Krevelen, *Coal: Typology-Physics-Chemistry-Constitution*, 3rd ed., Elsevier (1993).
2. J. G. Speight, Ed., *Fuel Science & Technology Handbook*, M. Dekker, New York (1992).
3. C. E. Snape, Ed., *Geochemistry. Characterisation and Conversion of Oil Shales*, NATO ASI series Vol. C455, Kluwer (1995).
4. M. L. Poutsma, *Energy & Fuels*, **4**(2), 113, (1990) and references therein.
5. A. C. Buchanan III and C. A. Biggs, *J. Org. Chem.* **54**, 517, (1989).
6. P. F. Britt and A. C. Buchanan III, *J. Org. Chem.* **56**, 6132, (1991).
7. S. C. Mitchell, C. J. Lafferty, R. Garcia, K. Ismail, C. E. Snape, A. C. Buchanan III, P. F. Britt and E. Klavetter, *Energy & Fuels*, **7**, 331, (1993).
8. K. Ismail, S. C. Mitchell, S. D. Brown, C. E. Snape, A. C. Buchanan III, P. F. Britt D. Franco and J. Yperman, *Energy & Fuels*, **9**, 707, (1995).
9. S. C. Mitchell, C. E. Snape and K. D. Bartle, *Fuel*, **73**, 1159, (1994).
10. C. E. Snape, S. C. Mitchell, K. Ismail and R. Garcia, *Euroanalysis V111: Reviews on Analytical Chemistry*, Royal Society Chemistry, (1994), p. 103.
11. K. Ismail, O. Sirkecioglu, J. M. Andersen, S. D. Brown, P. J. Hall, C. E. Snape and W. Steedman, *Polymer*, accepted for publication.
12. S. D. Brown, K. Ismail, C. E. Snape, A. Harding and K. M. Thomas, *Energy & Fuels*, **9**, 1104, (1995).
13. K. Ismail, G. D. Love, S. C. Mitchell, S. D. Brown and C. E. Snape, *Prepr. Am. Chem. Soc. Div. Fuel Chem.*, **39**(2), 551, (1994).
14. K. Ismail, S. D. Brown, O. Sirkecioglu, C. E. Snape, D. V. Franco, I. I. Maes and J. Yperman, *Proc. 8th Int. Conf. Coal Science*, Vol. 1, (1995). p.351, Elsevier Science Amsterdam.
15. I. M. Smith, PAH from coal utilisation - emissions and effects, *IEA Coal Research Report No. ICTIS/TR29*, London, UK, 1984.
16. C.V. Knight, M. S. Graham and B. S. Neal, in *Polynuclear Aromatic Hydrocarbons : formation, metabolism and measurement, Seventh International Symposium on Polynuclear Aromatic Hydrocarbons*, Columbus, OH, USA, Batelle, 1983, pp 689-710.
17. A. R. Collier, M. M. Rhead, C. J. Trier, and M. A. Bell, *Fuel*, **74**, 362 (1995)
18. Y. Zaks, J. Lo, D. Raucher and E. M. Pearce, *J. Appl. Polymer Sci.*, **27**, 913, (1982).
19. H. Bar and Z. Aizenshtat, *J. Anal. Appl. Pyrolysis*, **265**, (1991).
20. P. F. Nelson, I. W. Smith, R. J. Tyler and J. C. Mackie, *Energy & Fuels*, **2**, 391 (1988)
21. P.J. Hall, M.M. Antxustegi and J.M.Calo, *Proc. Carbon '94*, p.442, Granada, Spain.
22. G.E. Maciel, I.S. Chuang, and L. Gollob, *Macromolecules*, **17**, 1081, (1984).
23. K. Hultsch, *Chem. Ber.*, **74**, 1539, (1941).
24. A.B. Turner, *Quart. Rev.*, **18**, 347, (1964).
25. A.J. Mackinnon, P.J. Hall and M.M. Antxustegi, *Fuel*, **73**, 113, (1994).
26. A.J. Mackinnon, P.J. Hall, C.E. Snape and P. Burchill, *Fuel*, **74**, 136, (1995).
27. O. Sirkecioglu, P. McQueen, W. Steedman and C. E. Snape, *Fuel*, submitted.

	Normal PF	Anthracene-containing resite
Volatile Matter (% w/w)	40	58
Tar (% w/w resin)	25	34
Aromatics (% w/w resin)	10	20
Anthracene (% w/w resin)	1.8	7.0
Anthracene (% aromatics)	18	34
2-ring (% aromatics)	25	9
3-ring (% aromatics)	64	85
4-ring (% aromatics)	9	5
5-ring (% aromatics)	2	1

Table 1 : Yields from fluidised-bed pyrolysis of resites

	Normal PF	Anthracene-containing resite
Naphthalene	6	9
Acenaphthene	4	3
Acenaphthylene	10	27
Fluorene	6	16
Anthracene	1.2	0.8
Fluoranthene	16	40
Pyrene	12	34
Benzantracene	9	28
Chrysene	8	15

Table 2 : Mass ratios of phenanthrene to other PAH in fluidised-bed pyrolysis tars

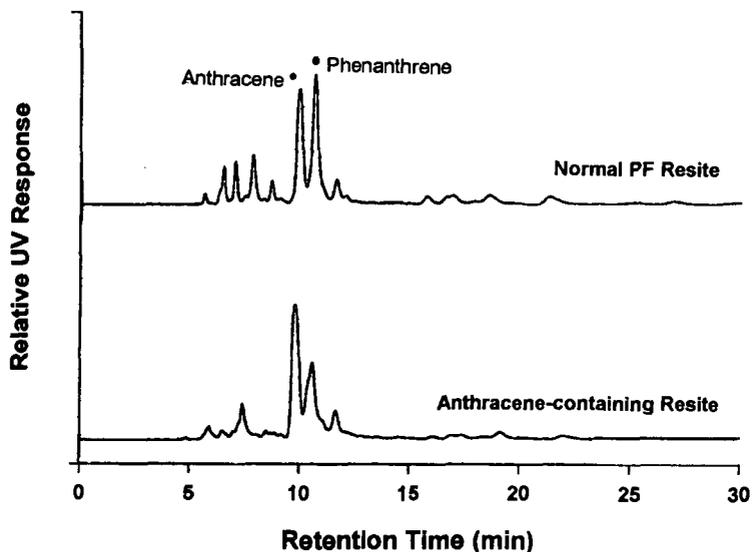


Figure 1 : HPLC traces of the aromatic fractions obtained from fluidised-bed pyrolysis of normal PF resite (top) and 9-(4-hydroxybenzyl)anthracene-containing resite (bottom)