

MEASUREMENT AND MODELLING OF REACTIVITY OF INDUSTRIAL PITCHES

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Introduction

This study was initiated due to the variance in product quality arising from the sourcing constraints currently placed on binder pitch production coupled with the inadequacy of standard empirical industrial parameters to reflect the chemical composition and behavior of such materials. In effect, is there a relationship between known physical properties and reactivity that we can predict the behavior of selected pitches.

Large ring polyaromatic hydrocarbons (PAHs) present the largest contribution to the desirable properties of coal tar pitches as binder pitches in preference to their petroleum analogues. High performance liquid chromatography (HPLC) is a common analytical method for the separation and identification of PAHs, having been successfully applied to a range of fuel-related materials including coal tars and liquids [1] and industrial pitches [2].

Experimental

Instrumentation The pitch fractions were analyzed using a Waters 600E HPLC coupled to a Waters 991 photodiode array detector (dad) operated at a spectral range of 200-500 nm. The column utilized was a Chromegabond RS column; the stationary phase was dinitroanilino propyl (DNAP), 5 μ , 60Å. This column operates by a charge transfer mechanism, which has proven extremely useful for separating condensed ring aromatic molecules. The mechanism of separation involves the delocalization of electrons between the support material and the π -electron rich PAH. A solvent gradient of n-hexane to DCM was operated at a flow of 1 ml/min and samples solubilized in methylene chloride at appropriate concentrations.

The column elute was analyzed by a full spectrum UV photodiode array detector and compound identification performed in two ways; direct UV spectra matches to previously injected standards (a library of over 60 PAH components has been created here at Penn State) and comparison of UV spectra to literature values.

The samples examined and reported here were the quinoline soluble material from one commercial and three

unknown coal tar pitches and a commercial petroleum pitch. Relevant data are provided in Table 1.

Sample	Softening Point (°C)	β resin (wt %)	QI (wt%)
Petroleum Pitch	122	7	0
Coal Tar Pitch	113	14	14
A1	94	10	15
A2	89	12	13
A3	100	15	17

Table 1. Properties of Industrial Pitches Examined by HPLC.

Results and Discussion

Figures 1 and 2 show the HPLC chromatograms of coal tar pitch quinoline soluble material. All four coal tar pitch samples demonstrated excellent separation with good molecular identification. As anticipated, there were minimal alkylated analogues of normal PAH. Generally, the 6 to 14 minute region comprised 3- and 4-ring components such as chrysene, fluoranthene and benzofluoranthenes. Components eluting in the 14 to 23 minute portion of the chromatogram are 5-6 ring aromatics such as benzopyrenes, perylene, indeno(1,2,3-cd)pyrene and benzo(g,h,i)perylene, which demonstrate strong absorbance and therefore present in high concentrations. All compounds thus far were positively identified by UV spectral comparison with standards, however the final region of the chromatogram is less well defined. At α 23.2 min, the peri-condensed compound coronene was identified in addition to its 10-ring analogue ovalene [retention time 32 min]. The series of intermediate peaks have been unresolvable for a variety of reasons. With PAH of ≥ 6 rings, the number of isomers, not including alkylated and hydrogenated analogues, is tremendous, therefore many of the components identified in the far region of the chromatogram have been interpreted with the aid of literature values and UV spectra. These include dibenzo(cd,lm)perylene [27 min], peropyrene [retention time 30 min] and benzo(a)naphtho(8,1,2-bcd)perylene [32.5 min]. One notable observation was that UV spectra from peaks in

this region were well defined and therefore not attributable to column bleed or noise.

Petroleum pitch, by its nature (no QI material) undergoes less severe processing during manufacture and hence exhibits less aromaticity and large ring PAHs. The chromatogram in Figure 3 demonstrates the relatively few large PAH compounds inherent to this material. The lower region, whilst again exhibiting 4- and 5-ring species, fewer were readily identifiable as normal PAH (chrysene, pyrene and benz(b)fluoranthene); more substitution, alkyl and hydro, was present. From 14 min, the components benzo(a)pyrene, benzo(e)pyrene and benzo(g,h,i)perylene eluted in sequence, the latter proving to be the heaviest species present.

Conclusions and Future Work

HPLC fingerprinting reported in this study confirms the trends observed by Martin et al. [3]. In assessing the fundamental differences in the carbonization reactivity and chemistry of different pitches, chemical and geometric factors must be taken into consideration. For example, it is well established that the ability to form flat, disc-shaped molecules is an important factor in the development of mesophase during carbonization. Such molecular configurations may not be inherent in the condensed structures arising from peri-condensed coronene and ovalene-types species. However, the nature of large PAH makes it impossible to physically obtain all samples for experimental examination.

Structural modelling is being performed using Alchemy and Cache software, which allows construction of graphical representations of selected models. The program takes account of steric factors including torsional deformation, van der Waals forces and out-of-plane bending imposed by the method of ring condensation. These theoretical models are hoped to go some way to explaining the physico-chemical properties of industrial pitches [4].

Acknowledgements

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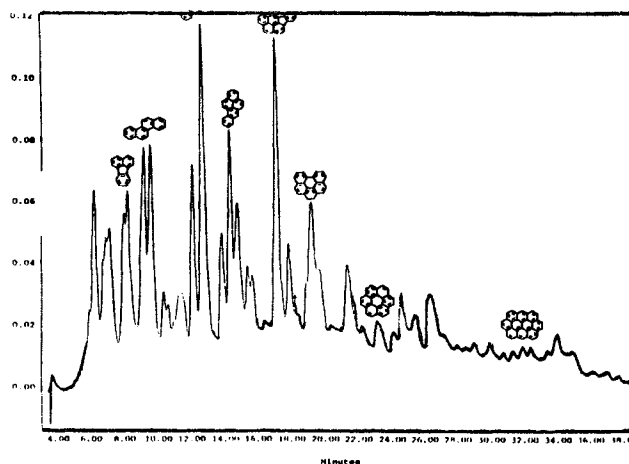


Figure 1. HPLC Chromatogram at Maximum UV Absorbance of Coal Tar Pitch Quinoline Soluble Material.

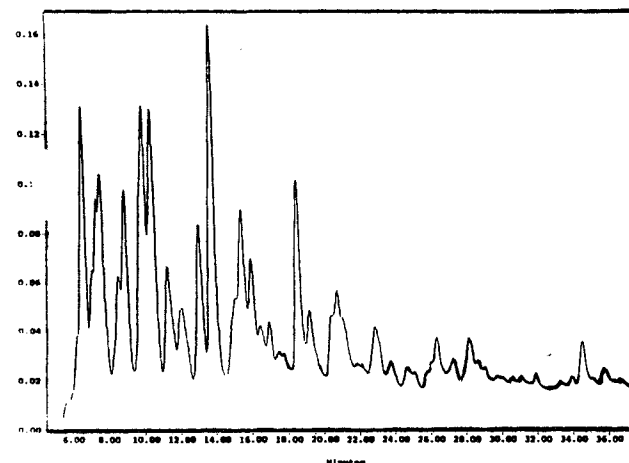


Figure 2. HPLC Chromatogram of Coal Tar Pitch A3 at Maximum UV Absorbance.

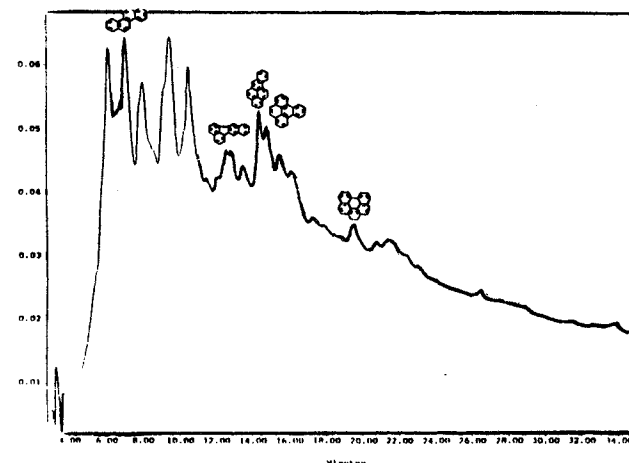


Figure 3. HPLC Chromatogram of Petroleum Pitch at Maximum UV Absorbance.