

PROPERTIES AND MOLECULAR STRUCTURE OF PITCHES FROM COPYROLYSIS PRODUCTS OF GOYNUK OIL SHALE AND AVGAMASYA ASPHALTITE

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Introduction

Pitch is a complex material comprised of thousands of components, mainly polyaromatic hydrocarbons and their heterocyclic analogs. Due to the complexity of pitch, very few analytical techniques provide much information about composition [1]. However, size exclusion chromatography (SEC) is a valuable analytical technique for the analysis of complex materials such as pitches. SEC separates molecules based on size, but with appropriate calibration procedures, can be used to provide molecular weight distribution data for pitch materials [2]. 1-methyl-2-pyrrolidinone (NMP) offers a number of advantages as a mobile phase. Much more material is dissolved in NMP and solute-column packing interactions common with SEC solvents such as tetrahydrofuran (THF) are much reduced. In this study, the molecular structure of pitches produced by air-blowing, N₂-blowing, and vacuum distillation of tars derived from copyrolysis of Goynuk oil shale (GOS) and Avgamasya asphaltite (AA) are characterised by different analytical techniques.

Experimental

The molecular structure of an air-blown pitch for 1.5hrs at 270°C (S5A5-Air), a nitrogen-blown pitch for 4hrs at 250°C (S5A5-N₂), and a vacuum distilled pitch (S5A5-V) derived from 50%GOS-50%AA tar, and a vacuum distilled pitch (S7A3-V) derived from 70%GOS-30%AA tar were investigated by SEC (using NMP with UV and RI detection), softening point, and aromaticity. Pitch samples were extracted with hexane and all hexane-solubles (extract), insolubles (residue) and original pitch were dissolved in NMP and were investigated by SEC. SEC was performed on a Polymer Labs Mixed E Bed column (polyvinylbenzene copolymer packing) with an attached guard column, with NMP pumped at 0.5 ml min⁻¹ as mobile phase. UV absorption at 298 nm (Severn Analytical SA6504 Programmable UV-absorption detector) and refractive index detection (ERMA ERC-

7520 type RI detector) provided detection of the samples. The system was operated at 80 °C and 108 bar. Injection was via a Rheodyne 7125 valve with 20µl sample loop.

Results and Discussion

Table 1 shows the general properties of the pitches studied. The SEC chromatograms for the S5A5-Air pitch, extract, and residue obtained with UV and RI detection, respectively, are presented in Figure 1. There is a significant shift to higher masses for the residues compared to extracts. For example, for S5A5-Air pitch, the lower MW peak maximum when compared with polystyrene standards corresponds to 300, while the corresponding peaks for the extract and residue are at 500 and 2000, respectively. The apparent molecular weight distribution for the residue is between 200-8000 for UV detection, and 200-16000 for RI detection. Both extract, residue and original pitch showed evidence of eluted material above 20000 by UV detection. The proportions of retained and excluded material vary with the sample. The peaks apparently shift to the higher masses if RI detection is employed. This is thought to be due to material with low UV absorbance and higher MW which is more prominent in the RI chromatogram.

Conclusions

This work has shown that size exclusion chromatography in NMP is suitable for characterising pitch materials. A significant shift to higher masses for the residue compared with the extracts is found. The findings indicate that all the pitch materials contain molecules which elute at or near the exclusion limit of the SEC column, when a sufficiently powerful solvent is used.

References

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Table 1. General properties of the pitches.

Pitches	C (wt%)	H (wt%)	N (wt%)	S (wt%)	O ^a (wt%)	H/C	CY (wt%)	SP (°C)	TI (wt%)
S5A5-Air	85.65	8.65	0.75	3.10	1.85	1.21	19.8	130	26.35
S5A5-N ₂	86.05	10.00	0.35	2.90	0.70	1.39	16.7	45	7.79
S5A5-V	83.90	10.30	0.90	2.85	2.05	1.47	13.4	55	1.00
S7A3-V	83.75	10.45	1.15	3.15	1.50	1.50	12.4	55	3.51

CY: carbon yield, SP: softening point, a: by difference

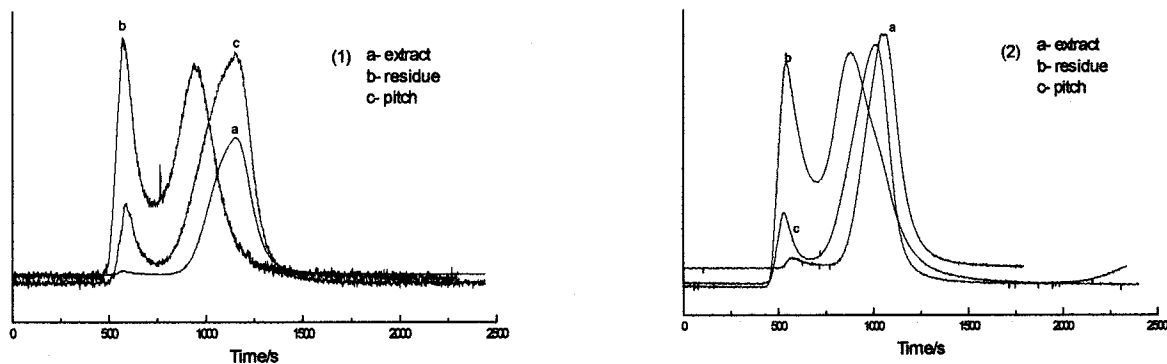


Figure 1. SEC chromatograms of S5A5-Air pitch, extract, and residue obtained from UV(1) and RI(2) detections.