FRACTIONATION OF PITCHES BY GEL PERMEATION CHROMATOGRAPHY

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Introduction

Gel permeation chromatography (GPC) is a valuable analytical technique for the analysis of complex materials such as pitches. GPC separates molecules based on size, but with appropriate calibration procedures, can be used to provide molecular weight distribution data for pitch materials. In previously reported work, measurement of the molecular weight distributions by GPC has been shown to be useful in differentiating some commercial pitches obtained from various precursors and with different processing histories [1]. In this present study, we have used the capabilities of GPC to characterize a wider variety of pitches and to separate these pitches into fractions of different molecular size. Chemical characterization was carried out on the individual fractions.

Experimental

We examined several different pitches including those derived from petroleum decant oil, pyrolysis tar, coal tar, anthracene, and naphthalene. Pitches were analyzed by GPC at elevated temperature (90°C) using a DuPont 850 chromatograph connected to a Knauer high-temperature differential refractometer. 1,2,4 -Trichlorobenzene (TCB) was pumped at 1.0 mL/min. through four Waters μ-Styragel columns (1000Å, 500Å, 500Å, 100Å). The system was calibrated using fractions from a pyrolysis tar. The tar had been separated using distillation and solvent extractions, and the molecular weight, Mn, of each fraction had been determined using vapor-phase osmometry. For the fractionation study, samples were collected at 5 mL intervals. Each fraction was further analyzed by GPC, ^{1}H FT-NMR, and ESR.

Results and Discussion

The properties of the pitches used for this study are summarized in Table 1 and examples of some of the GPC curves are shown in Figure 1. The power of GPC analysis can be seen in the differentiation between pitches of different sources. For example, the decant oil and pyrolysis tar-derived pitches have similar softening points and number-average molecular weights, but vastly different GPC curves. The pyrolysis tar pitch has a much broader molecular weight distribution and a less planar structure [2]. As a result, the pyrolysis tar pitch produces a more disordered carbon than the petroleum pitch derived from decant oil.

Table 1: Pitch Properties

Type	SP (°C)	MCC (%)	PI (%)	Mn	Mw
Naphthalene	120	62	7.9	352	546
Anthracene			3.0	233	313
Petroleum - Decant Oil	123	52	0.2	406	513
Pyrolysis Tar	122	47	0.0	420	857
QI-Free Coal Tar	132	61	21.4	291	366

The pitches in Table I were separated into eight to ten fractions based on retention time. Each fraction was reanalyzed by GPC. The fractions were narrow (average polydispersity of 1.08) and had number-average molecular weights that correlated well with the original curve as shown in Figure 2. Although the molecular weight distribution is narrower, each fraction is still a very complex mixture. We used ^{1}H FT-NMR to characterize all the fractions for each pitch. We found only small differences between the NMR spectra of the fractions indicating that the basic chemical structures did not change significantly with molecular size. We also attempted to characterize the fractions for some of the pitches using electron spin resonance (ESR). There was a general trend for increasing free radical concentration as the molecular weight increased.

Conclusions

GPC is a powerful technique for showing molecular weight distribution differences between pitches from different precursors. These differences can be correlated with other properties such as carbonization behavior. Fractionation by GPC is useful for separating pitches into narrower fractions which can then be utilized for more detailed analytical characterization.

Acknowledgment

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References

1. Mayer, H. K., in *Carbon '95 (Ext. Abstr. 22nd Biennial Conf. Carbon)*, San Diego, CA, 1995. pp. 202-203.
2. Dickinson, E. M., *Fuel*, 1980, 59, 290.

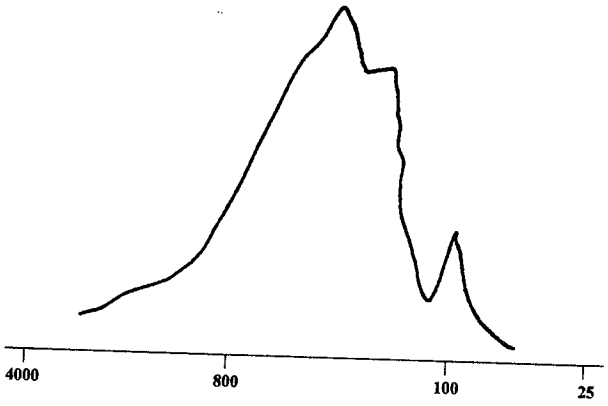

Figure 1a. GPC curve of naphthalene pitch.

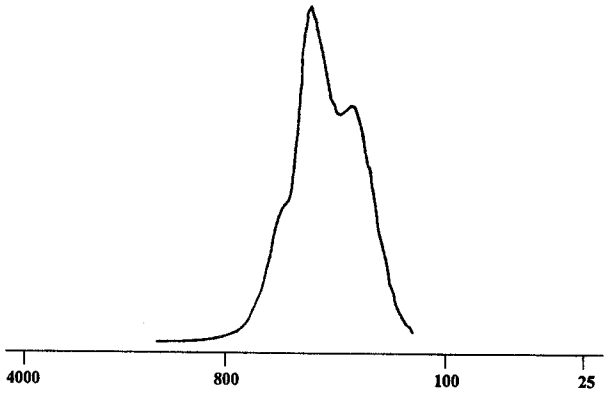

Figure 1b. GPC curve of petroleum-decant pitch.

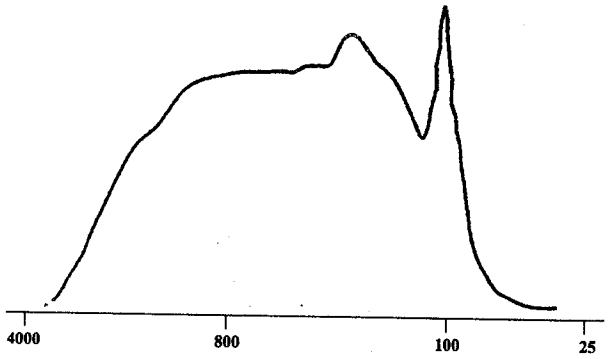

Figure 1c. GPC curve of pyrolysis tar pitch.

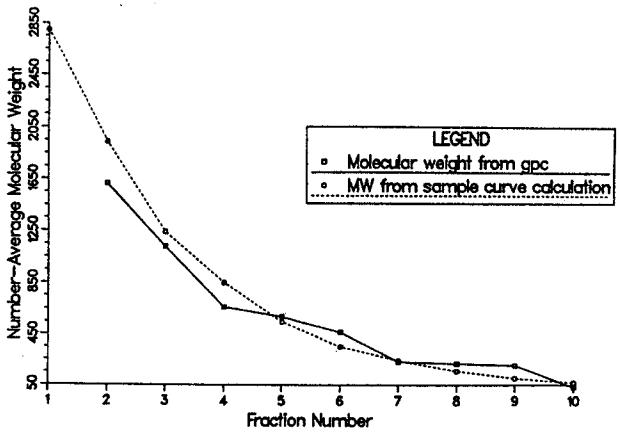

Figure 2. The molecular weight of the naphthalene pitch fraction is compared to the molecular weight extrapolated from the original sample curve.