

Isolating pitch oligomers by continuous, countercurrent, dense-gas extraction–Part I. Isotropic pitches of narrow molecular weight distribution

Eduardo G. Cervo, David F. Esguerra and Mark C. Thies*
Department of Chemical Engineering, Center for Advanced
Engineering Fibers and Films, Clemson University, Clemson, SC
29634-0909

Introduction

Petroleum pitches are produced by the thermal polymerization of aromatic decant oil, a by-product of the fluid catalytic cracking of the heavy gas oil fraction of crude oil. Depending upon their composition and properties, they can serve as precursors for manufacturing diverse advanced carbon materials [1]. In this work, a method known as dense-gas extraction (DGE) was investigated for the production of isotropic, dimer-rich pitches, suitable as precursors for activated carbon fibers, from a representative petroleum pitch of broad molecular weight distribution (M-50 from Marathon Petroleum Company LLC). As shown in Fig. 1, M-50 is oligomeric in nature with a mol. wt. that extends from approximately 200 to over 1000 [2]. The species themselves consist of alkylated polycyclic aromatic hydrocarbons (PAHs) [3]. In this work, two-column DGE was used to produce dimer-rich pitches from M-50. In addition to the effect of S/P ratio and $+\Delta T$, the pitch feed location and the use of other solvents under supercritical extraction (SCE) conditions were also considered.

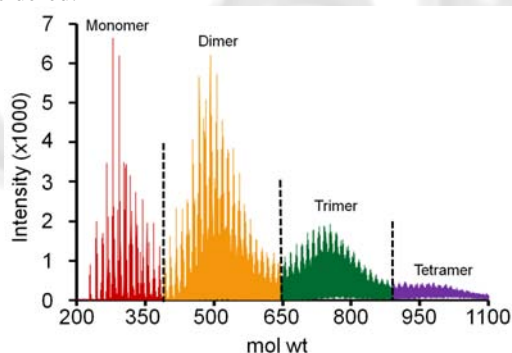


Figure 1. MALDI spectrum of M-50 petroleum pitch. Monomer species are defined as having a mol wt from 210 to 388, dimer from 388 to 645, trimer from 645 to 890, and tetramer from 890 to 1120 Da.

Experimental

Isotropic petroleum pitch M-50 (CAS 68187-58-6) was obtained from Marathon Petroleum Company LLC. HPLC-grade toluene (CAS 108-88-3) and pentane (CAS 109-66-0) with a stated purity of 99.9 % were obtained from Fisher Scientific and used as the extraction solvents. As shown in Fig 2, fractionation of M-50 pitch was carried out using two packed columns. Details of the design and construction of the apparatus are given elsewhere [4]. In a typical two-column experiment for producing dimer-rich pitches, the feed pitch was delivered to the lower 1/3 of the first column (Col-1)

packing in the molten state (at $\sim 300^\circ\text{C}$) at a flow rate of 69 g/h. Simultaneously, toluene was delivered to the bottom of Col-1 at a rate of 832 g/h via an HPLC pump. In this case, the solvent-to-pitch (S/P) ratio was 12.1/1. To improve selectivity, a positive temperature profile ($+\Delta T$) of 350°C (bottom section), 380°C (middle section) and 400°C (top section) was established along the length of Col-1. An increase in temperature decreases the solvent power, causing higher mol. wt. species to precipitate and form a second phase. The precipitate heavy phase then flows down the column, generating a reflux that improves the purity of the solvent-rich phase. The operating pressure, in both Col-1 and column 2 (Col-2), was controlled by means of a top regulating valve.

In general, solvent power was controlled by means of temperature, pressure, S/P ratio, and solvent composition. The solvent-rich phase, containing the extracted pitch oligomers, in this case monomer and dimer, was taken off as top product and then sent to an evaporator where the product was concentrated from 6 to 64 wt% pitch by removal of toluene solvent.

The resultant 64 wt% concentrated pitch solution was delivered to the lower 1/4 packing of Col-2 at 49 g/h. Pentane, the extractive solvent for Col-2, was delivered to the bottom of Col-2 at 643 g/h via an HPLC pump, followed by a preheater. A $+\Delta T$ was established along the height of Col-2 (i.e., top at 260°C , middle-1 at 255°C , middle-2 at 250°C , bottom and stillpot at 240°C). The solvent-rich phase containing monomer is taken off as top product, and the pitch-rich phase containing primarily dimer is taken off as bottom product. Pitch fractions produced by DGE were analyzed for absolute molecular weight using a Bruker Daltonics Autoflex matrix-assisted, laser desorption/ionization, time-of-flight (MALDI) mass spectrometer equipped with a 337 nm nitrogen laser. Instrument settings and sample preparation details are given elsewhere [5]. Reported softening points were obtained with a Mettler FP83HT Dropping Point Cell, equipped with softening-point cups.

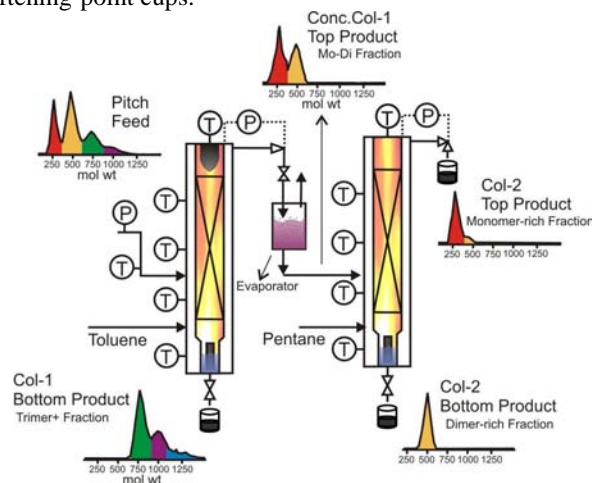


Figure 1. Fractionation of M-50 via two-column DGE to produce dimer-rich pitches. Spectra shown are actual MALDI spectra of feed pitch M-50 and extraction products obtained in this study.

Results and Discussion

To produce dimer via two-column extractions, Col-1 was operated at $+\Delta T_2$, S/P ratio of 12.1/1, 69.9 bar (1000 psig), and toluene as the SCE solvent to produce a monomer-dimer top product. Next, an evaporator was used to remove the toluene solvent and then increase the concentration of pitch in the solvent from 6 wt% to 64 wt%. In Col-2, both pentane and pentane-toluene mixtures were used to extract all monomer. The pitch-rich phase, mainly dimer, flows down the column and is collected as a bottom product. To separate monomer from dimer, different S/P ratios, pressures, temperatures, and solvent compositions were used. For instance, good selectivity was obtained when Col-2 was operated as a strip./rect. at $+\Delta T$ (270-260-250-240 °C), S/P ratio of 22/1, 69.9 bar (1000 psig), using pentane as the SCE solvent. As seen in Fig. 3, a sharp separation between monomer and dimer was achieved in Col-2, with impurities being less than 5 mol%. Composition values and softening point are shown in Table 1.

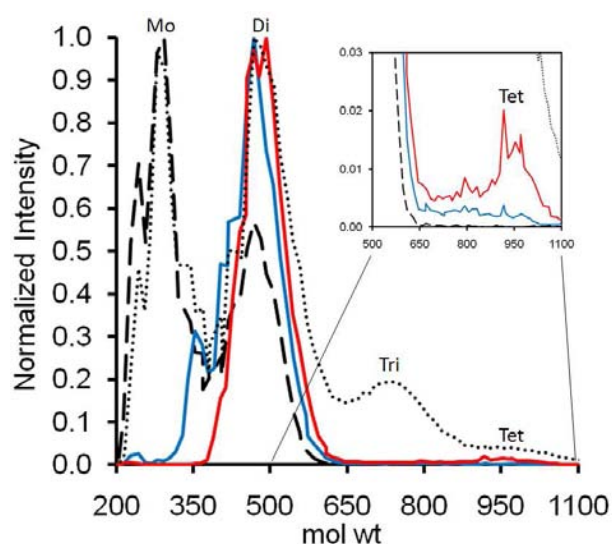


Figure 3. MALDI spectra of feed pitch M-50 to Col-1 (.....), Col-1 top product serving as the feed to Col-2 (---), and the dimer-rich bottom products Dimer A (—) and Dimer B (—). Spectra have been normalized (max peak height = 1) to facilitate comparison.

Table 1. Composition and softening point of selected pitches

Pitch	MALDI Area Fractions					Softening Point (°C)
	Mo	Di	Tri	Tet	Pent	
M-50	0.16	0.57	0.23	0.0	0.00	116.1 ± 0.8
Monomer A	0.96	0.04	0.00	0.0	0.00	41.1 ± 0.2
Dimer A ^a	0.03	0.96	0.01	0.0	0.00	170.3 ± 0.5
Dimer B ^a	0.00	0.96	0.01	0.0	0.00	216.7 ± 1.8
Dimer B	0.00	0.99	0.00	0.0	0.00	216.7 ± 1.8

In order to extract all monomer from the feed pitch to Col-2, and obtain a dimer-rich product of higher purity, other

extraction pressures, temperatures profiles, S/P ratios, and solvent compositions were investigated. Complete extraction of monomer from the feed pitch to Col-2 was obtained by operating Col-2 at $+\Delta T$ (270-260-250-240 °C), S/P ratio of 24, 69.9 bar (1000 psig), and 25/75 vol% toluene-pentane mixture as solvent. In this case, a 96+ mol% dimer-rich pitch (Dimer B) was produced at 9.3 g/h (overall yield of 0.14). Note that dimer B^a pitch shown in Table 1 was analyzed by MALDI using a solvent-based sample preparation method. Kulkarni et al. [6] have demonstrated that for such sample preparation method, the higher mol wt species are accentuated. Thus, on a solvent-free basis (Dimer B) was actually found to be a 99 mol% dimer-rich pitch, with minimal trimer+ impurities.

Conclusions

In this investigation, an oligomeric petroleum pitch (M-50) was fractionated using two continuous, counter-current, multistage, packed columns. Pure monomer and dimer were isolated using supercritical toluene in Col-1, while supercritical pentane was used in Col-2. Overall, monomer- and dimer-rich pitches with purities of up to 99 mol% were obtained on a continuous basis. Based on these results, M-50 was estimated to be 50 wt% monomer, 27 wt% dimer, and 23 wt% of trimer and heavier species. To our knowledge, this is the first time that the oligomers from an oligomeric pitch are quantified and dimer-rich pitches are produced in significant quantities for manufacturing carbon artifacts. In terms of applicability, such dimer-rich pitch precursors have satisfactory softening points and can be easily converted into carbon fibers.

Acknowledgments. Acknowledgments are made to the Basic Energy Sciences division of the United States Department of Energy, the Clemson University Center for Advanced Engineering Fibers and Films, the Donors of the American Chemical Society Petroleum Research Fund, and the Air Force Research Laboratory AFRL/RZSM.

References

- [1] Chung, Deborah D.L., Carbon Fiber Composites, 1st ed., Butterworth-Heinemann, Boston, 1994, Chapter 4.
- [2] W.F. Edwards, L. Jin, M.C. Thies, MALDI-TOF mass spectrometry: obtaining reliable mass spectra for insoluble carbonaceous pitches, Carbon 41 (2003) 2761–2768
- [3] Burgess, W. A.; Thies, M. C. Spectral Identification of the Monomeric Fraction of Aromatic Hydrocarbons Present in a Petroleum Pitch. Subm. for publication in Energy and Fuels, 2010.
- [4] W.F. Edwards, M.C. Thies, Fractionation of pitches by molecular weight using continuous and semibatch dense-gas extraction, Carbon 44 (2006) 243-252.
- [5] A. Cristadoro, S.U. Kulkarni, W.A. Burgess, E.G. Cerro, H.J. Räder, K. Müllen, D.A. Bruce, M.C. Thies, Structural characterization of the oligomeric constituents of petroleum pitches, Carbon 47 (2009) 2358-2370.
- [6]. S.U. Kulkarni, H.J. Räder, M.C. Thies, Investigation of solvent-based and solvent-free MALDI-TOF-MS sample preparation methods for the qualitative and quantitative analysis of petroleum macromolecules, J. Am. Soc. Mass Spectr., in preparation.