Isolating pitch oligomers by continuous, countercurrent, dense-gas extraction–Part II. Mesophase pitches of narrow molecular weight

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Introduction

Petroleum pitches are carbonaceous materials that can serve as precursors for high performance/high thermal conductivity carbon fibers. They are complex mixtures of alkylated polycyclic aromatic hydrocarbons (PAHs) with molecular weight ranging from 200 to over 1000 Da [6] and are obtained by the thermal polymerization of aromatic decant oil, a byproduct of the fluid catalytic cracking (FCC) of the heavy gas oil fraction of crude oil. Mesophase pitch-based carbon fibers, i.e., those processed from anisotropic liquid-crystalline pitches, present attractive properties such as high thermal conductivity (up to four times that of copper), low density and low coefficient of thermal expansion [1], for thermal management applications where thermal stresses must be minimized and excess heat needs to be efficiently removed: examples include microelectronic packaging, semiconductor modules and hybrid cars [2]. In this work, our dense-gas extraction (DGE) process is investigated for producing mesophase pitches for advanced carbon application from a petroleum pitch (M-50, from Marathon Petroleum Company LLC).

Experimental

As shown in Fig. 1, fractionation of M-50 pitch was carried out continuously using two packed columns in series. M-50 pitch is oligomeric in nature, and its MWD ranges from 200 to over 1000 Da. M-50 actual mass spectrum is shown in Fig. 1 adjacent to column 1 (Col-1) feed stream. Recent work by our group at Clemson has identified the predominant monomeric species present in M-50 [3] and elucidated possible structures for the higher molecular weight species [4]. Some representative structures are shown in Fig. 2.

In a typical two-column experiment for producing mesophase pitches the feed pitch is delivered to the lower 1/3 of Col-1 packing in the molten state (at ~300 °C) at a flow rate of 69 g/h. Simultaneously, toluene is delivered to the bottom of Col-1 at a rate of 832 g/h via an HPLC pump. The solvent-to-pitch (S/P) ratio is varied between 8 and 12.1/1 and pressure is set to 1000 psig. A positive temperature profile (+ΔT) of 330°C (bottom section), 350°C (middle section) and 380°C (top section) is established along the length of Col-1. The solvent-rich phase, containing the extracted pitch oligomers, in this case monomer, dimer and trimer, is fed directly into column 2 (Col-2), where extraction of monomer and dimer results in a bottom product comprised of dimer, trimer, and little tetramer. This bottom product, a trimer-rich pitch, will have different amounts of mesophase depending on its composition. Lastly, note that the operating pressure in Col-2 is lower than Col-1, so that the top product of Col-1 can flow into Col-2. Additional details of the design and construction of the apparatus are given elsewhere [5].

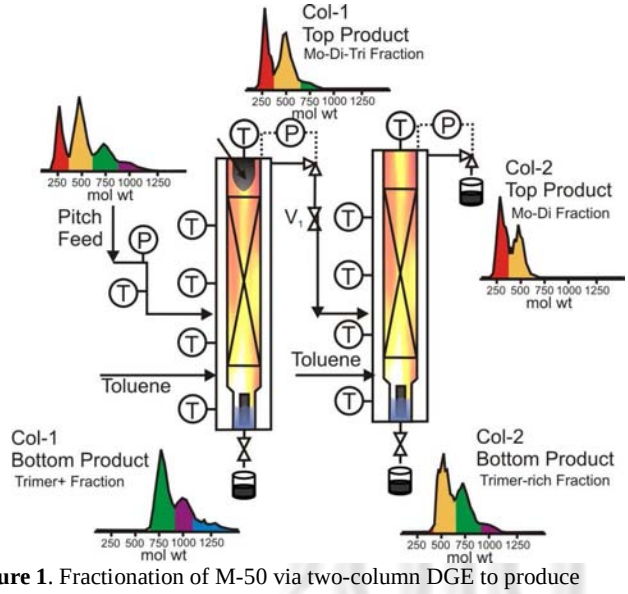

Figure 1. Fractionation of M-50 via two-column DGE to produce mesophase pitches. Spectra shown are actual MALDI spectra of feed pitch M-50 and extraction products obtained in this study

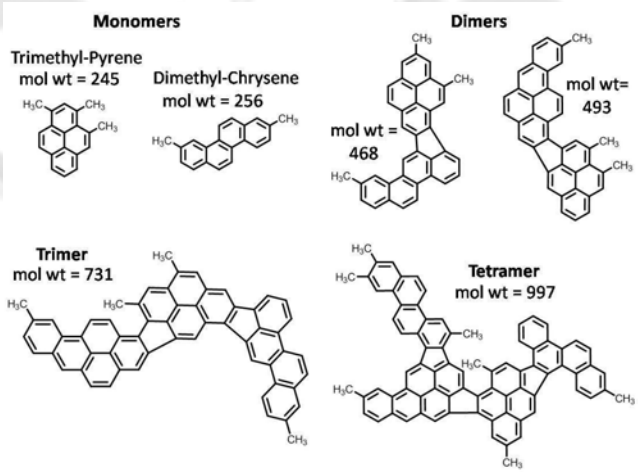

Figure 2. Representative M-50 pitch species

Pitch fractions produced by SCE were analyzed for absolute molecular weight and mol fractions 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 [6]. Reported softening points were obtained with a Mettler FP83HT Dropping Point Cell, equipped with softening-point cups.

Results and Discussion

By operating Col-1 at +ΔT, S/P ratio of 8.0, and 69.9 bar, a top product comprised of 15 mol% trimer, 19mol% monomer, 35 mol% dimer and minimal tetramer (1 mol% or lower) is obtained. This top product from Col-1, containing 10 wt% pitch, was then sent to Col-2, where the S/P ratio was kept constant and both pressure and temperature profiles were varied in order to control the solvent power and selectivity of the extraction.

In order to reduce the dimer content in the bottom product and obtain a trimer-rich product of even higher purity, the extraction pressure in Col-2 may be raised above 60 bar. However, as seen in Fig. 3, some trimer is already observed in the extract at 60 bar, so an increase in pressure would not only cause even more trimer species to be extracted, but would also significantly decrease the overall yield of trimer-rich pitch obtained as bottom product in Col-2. To improve selectivity at higher pressures, the temperature profile was raised by 20 °C in the upper sections of Col-2 (+ΔT of 400-400-350-350 °C). However, higher temperatures not only increase the dimer content in the bottom product (Trimer B), but also more tetramer is obtained than when operating at +ΔT (380-380-350-350 °C), 60 bar (Trimer A). Note also that when Col-2 is operated at +ΔT (380-380-350-350 °C) and 60 bar (Trimer A), the tetramer content is reduced, when compared to the bottom product from the one-column DGE (Trimer C), but not eliminated due to (1) thermal polymerization of dimer into tetramer inside Col-2 and (2) tetramer impurities present in the feed pitch to Col-2 (i.e., top product from Col-1). Compositions and softening points are shown in Table 1.

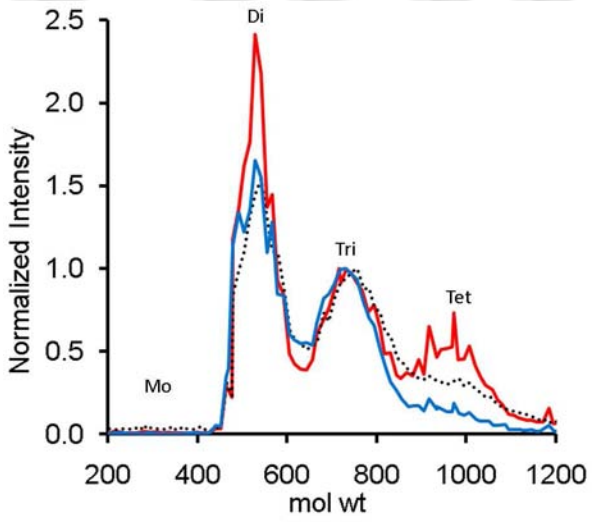

Figure 3. MALDI spectra of trimer-rich bottom products. Trimer A from Col-2 at +ΔT (380-380-350-350 °C), S/P = 17/1, 60 bar (——), Trimer B from Col-2 at +ΔT (400-400-350-350 °C), S/P = 17/1, 63 bar (——), and Trimer C from Col-1 at +ΔT_2, S/P = 12.1/1, 69.9 bar (·····). Spectra have been normalized to trimer content (max peak height = 1) to facilitate comparison.

Table 1. Composition and softening point of selected pitches produced in this work.

Pitch	MALDI Area Fractions					Softening Point (°C)
	Mo	Di	Tri	Tet	Pent	
M-50	0.16	0.57	0.23	0.04	0.00	116.1 ± 0.8
Trimer A	0.00	0.28	0.60	0.11	0.01	286.1
Trimer B	0.00	0.19	0.42	0.36	0.03	319.1 ± 0.5
Trimer C	0.00	0.24	0.49	0.22	0.05	332.8 ± 1.3

Even though only 60 mol% trimer-rich pitches have been produced, work is underway in our laboratory to optimize the conditions in both Col-1 and Col-2 so that trimer-rich pitches of higher purities can be obtained at higher overall pitch yields. By reducing tetramer and heavier species content, trimer-rich pitches of high purity are expected to have softening points close to 250 °C

Conclusions

A two-column extraction setup using supercritical and toluene was used to produce a trimer-rich pitches of up to 60 mol% purity from a feed of oligomeric, M-50 petroleum pitch. These mesophase pitches have softening points between 286 and 333 °C and are expected to be ideal precursors for carbon fibers for thermal management applications because (1) they would require less time for stabilization and (2) since trimer species are comprised of relatively large PAHs, they would form highly oriented fibers, which in turn would improve physical properties of the processed fibers.

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