ISOLATING PITCH OLIGOMERS BY CONTINUOUS, COUNTERCURRENT, DENSE-GAS FRACTIONATION

Eduardo G. Cervo, Mark C. Thies, Dept. of Chemical Engineering,
Center for Advanced Engineering Fibers and Films, Clemson University, Clemson, SC, 29634-0909

Abstract

Dense-gas extraction (DGE) was used to fractionate an isotropic petroleum pitch (number-average molecular weight ($\overline{M}_n$) = 516) into oligomeric cuts. A countercurrent-flow packed column was used to effect the separation, with supercritical toluene being used as the dense-gas solvent and commercially available M-50 or A-240 pitch being used as the feed. Isothermal operation at 330, 350, and 380 °C was investigated, as well as operation with a linear positive temperature gradient (+ΔT), with the bottom of the column at 330 and the top at 380 °C. For isothermal operation, the molecular weight distribution of the bottom products consisted primarily of dimer ($\overline{M}_n$ = 508) and trimer ($\overline{M}_n$ = 759) species, with pressure changes of as little as 5 bar producing significant changes in their relative distribution, as observed by MALDI mass spectrometry. On the other hand, by operating with a +ΔT we could produce a bottom product consisting primarily of trimers and tetramers ($\overline{M}_n$ = 997).

Keywords: Carbon precursor, Petroleum pitch, Mesophase

1. Introduction

Petroleum pitches contain 90-95% carbon by weight and are potential precursors for advanced carbon materials, such as activated carbon fibers and high thermal conductivity carbon-carbon composites [Basova 2005, Beauharnois 2001]. They are produced by the thermal polymerization of an aromatic oil feedstock, are oligomeric in nature, and have a mol wt range of ~250 to just under 2000. In general, petroleum pitches are polycyclic aromatic hydrocarbons with methyl and naphthenic substitution [Dickinson 1985, Mochida 1995]. The mass spectrum of M-50, a commercially available pitch from Marathon Petroleum Company LLC, and molecular structures suggested by our group are shown in Figure 1.
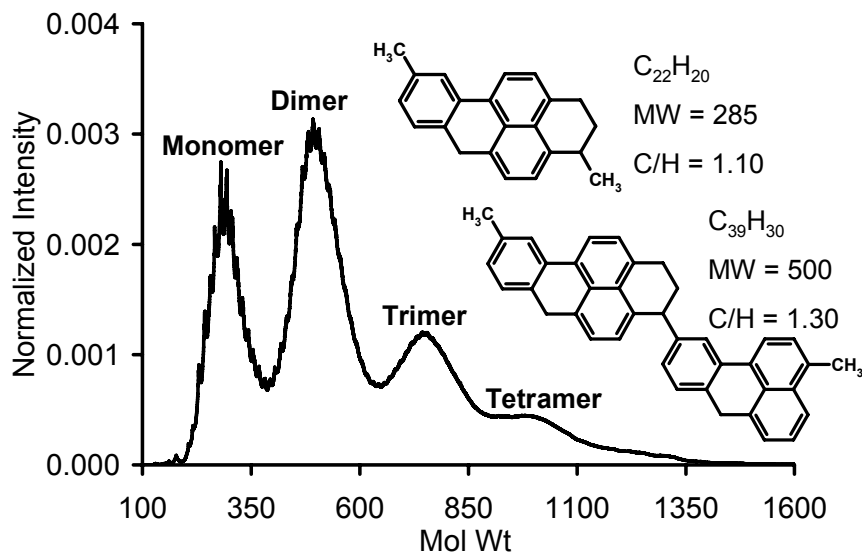

Figure 1. MALDI mass spectrum of M-50 petroleum pitch
and suggested structures for typical monomer and dimer species.

Previous investigations have recognized the influence of the molecular weight (mol wt) of pitches on the physical properties of pitch-based carbon materials, but controlling and measuring the mol wt of these precursors has long been a difficult task. To this end, our group is investigating the use of dense-gas extraction (DGE) for the fractionation of petroleum pitches [Edwards 2005, 2006], with the goal of controlling its oligomeric composition, using supercritical toluene (T_c = 318.6 °C, P_c = 41.1 bar) as the extractive solvent. With the advent of matrix-

assisted laser desorption–ionization time-of-flight mass spectrometry (MALDI) and its application to pitches [Edwards 2003], our group is now able to quantify the effect of extraction conditions, such as pressure and temperature, on the oligomeric composition of extracted materials.

2. Experimental

2.1. Materials

M-50 (CAS 68187-58-6) isotropic petroleum pitch, with reported softening point from 104-124 °C, was obtained from Marathon Petroleum. The pitch was received in pellet form and used without further modification. HPLC-grade toluene (CAS 108-88-3) with a stated purity of 99.9% was obtained from Fisher Scientific. For MALDI analysis, 7,7,8,8-tetracyanoquinodimethane (CAS 1518-16-7) was obtained from TCI America.

2.2. Experimental Apparatus and Procedure

Dense-gas extraction of the pitches was carried out using a setup designed for continuous operation at temperatures to 400 °C and pressures to 200 bar, see Figure 2. As a detailed discussion of the apparatus and procedure is given elsewhere [Edwards 2006], a truncated description is given here. The central feature of the apparatus is a countercurrent, multistage packed column, which has a total height of 2.03 m and an inner diameter of 1.8 cm. 1.47 m of the column length is filled with 4-mm random packing. The temperature of the column can be controlled for either isothermal operation or a positive temperature gradient from the bottom to the top of the column.
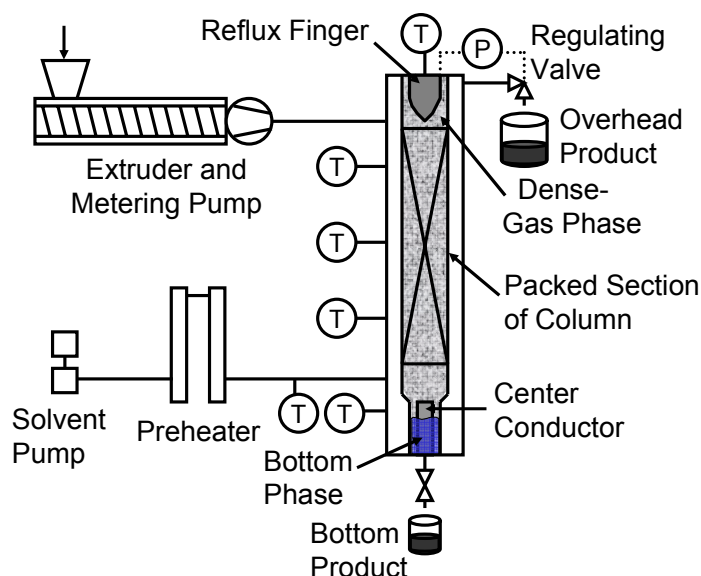

Figure 2. Dense-gas extraction apparatus for continuous fractionation of pitches. Adapted with permission from *Carbon*, 2006. Copyright Elsevier.

For a typical DGE run, the feed pitch is delivered to the top of the column in the molten state (T ~300 °C) at a flow rate of 117 g/h via a single-screw extruder and metering pump. The dense-gas solvent (in our case toluene) is compressed to column operating pressures via an HPLC pump, preheated, and delivered to the stillpot (i.e., the section of the column below the packing) at a rate of 598 g/hr. Thus, a constant solvent-to-pitch (S/P) ratio of 5.1/1 was used for all experiments. As the solvent flows up and the pitch flows down the column (due to density differences), lower mol wt species are stripped out of the pitch feed and into the solvent phase. In addition, a fraction of the compressed, dense-gas solvent is absorbed into the pitch phase. Thus, a solvent-rich phase containing extracted pitch species is taken off as top product, and a pitch-rich liquid phase containing the unextracted pitch species is taken off as bottom product.

2.3 MALDI Analysis

Pitch fractions produced by DGE were analyzed for absolute molecular weight using a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer. The instrument was calibrated with a mixture of peptides available from Bruker Daltonics and operated in the reflector mode for all analyses.

For sample preparation, approximately 10 mg of a given analyte was combined with 200 mg of the matrix TCNQ, and the two were mixed together for 5 min using a grinding mill. A thin film of the powder obtained was then deposited onto a target cell using a technique developed in our laboratory and explained in detail elsewhere [Edwards 2003].

3. Results and Discussion

3.1 Effect of solvent power on yield and composition

The effect of DGE operating temperature and pressure on the fraction of the feed pitch that is not extracted and ends up as bottom product (i.e., the bottom-product pitch yield) is shown in Figure 3. The solvent-to-pitch (S/P) ratio was held constant at 5.1/1 for all runs shown. Isothermal operation of the DGE extraction process at 330 and 350 °C is shown, as well as operation with a linear positive temperature gradient (+ΔT), with the bottom of the column (including the stillpot and bottom third of packing) at 330, the middle third of packing at 350, and the top third of packing and reflux finger at 380 °C. As seen from the three mixture isotherms, higher operating pressures (and the commensurate increase in pure solvent densities) result in increased extraction of the pitch into the solvent phase, and thus lower bottom-phase pitch yields. The dramatic decreases in yields that occur at 330 and 350 °C take place near the critical points of the mixtures [Schneider, 1980]. A more complex yield behavior is observed when a +ΔT (labeled as "330-380" in Figure 3) is used.
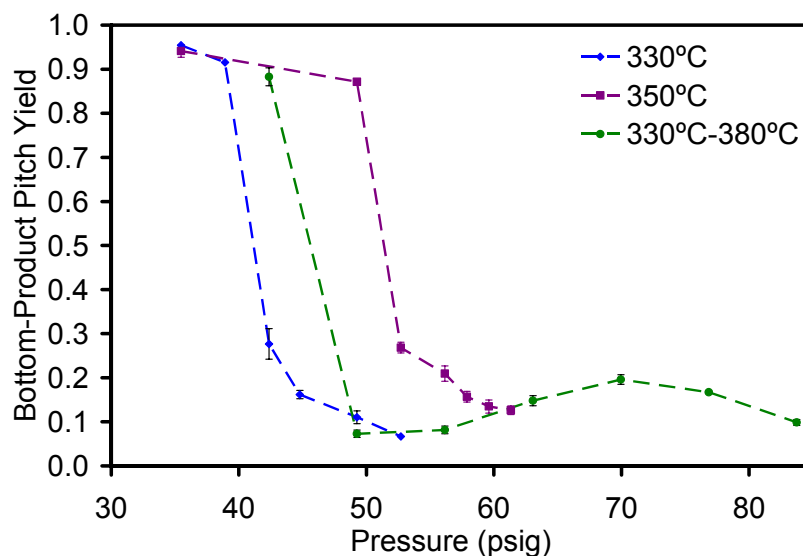

Figure 3. DGE bottom-product pitch yield for both isothermal and +ΔT operation.

3.2 MALDI spectra of DGE bottom products

MALDI mass spectra of the bottom products generated by DGE at both isothermal and +ΔT conditions are given in Figures 4 and 5. Results are presented here in terms of normalized instrument intensity, with the total area under each curve summing to one. Thus, the curves shown give mol wt distributions and $\overline{M}_n$ based on area, and not on mass or mole number. We note, however, that work in progress by our group has established that peak height/area is a good first approximation of mole number/fraction.

An example of the changes in the oligomeric composition of bottom products that occur with increasing operating pressure during isothermal DGE operation is given for 350 °C in Figure 4. Comparing these results to Figure 3, we see that significant changes in the oligomeric makeup of pitch fractions can occur with only modest changes in the bottom pitch yield. This feature would be advantageous for a commercial process, as product yields need to be maximized.

As shown in Figure 5, completely different behavior is observed with a +ΔT: Increases in column pressure lead to increases in dimer and decreases in trimer and tetramer concentrations; furthermore, the $\overline{M}_n$ of the isolated fractions are significantly higher than for the isothermal case. The seeming paradox of a lower mol wt product and a higher product yield being obtained with increasing pressure can be explained in terms of the competing effects of solvent power and co-solvent interactions [Edwards 2006].
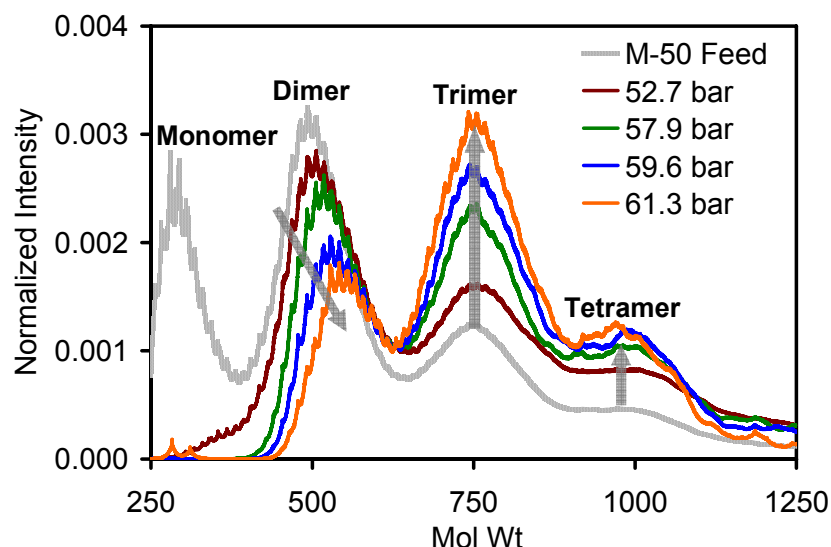
Figure 4. MALDI mass spectra of bottom products from isothermal dense-gas extraction at 350 °C. Increasing pressure increases the mol wt of bottom products. Reproduced with permission from *Chem. Eng. Tech.*, 2007. Copyright Wiley-VCH.
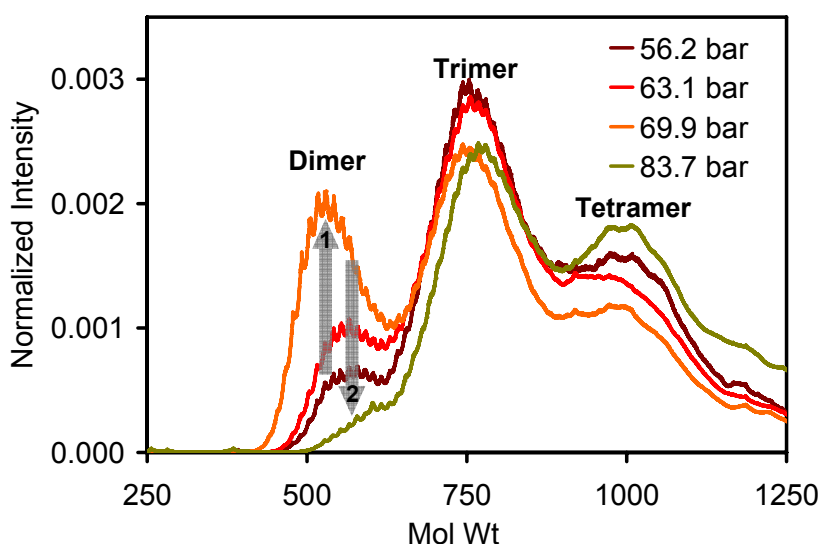

Figure 5. MALDI mass spectra of bottom products from a dense-gas extraction operating at a +ΔT. Mol wt of bottom products initially decreases (1) with increasing pressure followed by a increase in mol wt (2) at higher pressures.

4. Conclusions

Dense-gas extraction of Marathon's M-50 isotropic petroleum pitch was carried out countercurrently with the solvent toluene in a packed column under both isothermal and temperature-gradient conditions. Steady-state feed flow rates of the pitch and solvent to the column were held constant at a weight ratio of 5.1/1 for all runs. By operating the column either isothermally or with a +ΔT, product yields within the desired range can be obtained at specific operating pressures. However, if a +ΔT is used, yields are relatively constant and remain in the desired range over a surprisingly wide range of pressures.

References

Basova, Y. V.; Edie, D. D.; Badheka, P. Y.; Bellam H.-C. The effect of precursor chemistry and preparation conditions on the formation of pore structure in metal-containing carbon fibers. *Carbon* **2005**, *43*, 1533-1545.

Beauharnois, M. E. ; Edie, D. D. ; Thies, M. C. Carbon fibers from mixtures of AR and supercritically extracted mesophases. *Carbon* **2001**, *39*, 2101.

Cervo, E. G.; Thies, M. C. Control of the Molecular Weight Distribution of Petroleum Pitches via Dense-Gas Extraction. Chem. Eng. Tech. **2007**, accepted for publication.

Dickinson, E. M. Average structures of petroleum pitches fractions by ^{1}H/^{13}C n.m.r. spectroscopy. *Fuel* **1985**, *64*, 704-706.

Edwards, W. F.; Jin, L.; Thies, M. C. MALDI-TOF mass spectrometry: Obtaining reliable mass spectra for insoluble carbonaceous pitches. *Carbon* **2003**, *41*, 2761-2768.

Edwards, W. F.; Thies, M. C. Dense-Gas fractionation and MALDI characterization of carbonaceous pitches. *Energy Fuels* **2005**, *19*, 984-991.

Edwards, W. F.; Thies, M. C. Fractionation of pitches by molecular weight using continuous and semibatch Dense-Gas extraction. *Carbon* **2006**, *44*, 243-252.

Mochida, I. ; Yoon, S.-H ; Korai, Y.; Kanno, K.; Sakai, Y.; Komatsu, M. Carbon Fibers from aromatic hydrocarbons. *Chemtech* **1995**, 25 (2), 29.

Schneider, G. M., E. Stahl, G. Wilke. 1980. Extraction with Supercritical Gases. Verlag Chemie, Weinheim.