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# REPORT DOCUMENTATION PAGE

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|  |   |   |
|--|---|---|
| <b>1. REPORT DATE (DD-MM-YYYY)</b><br>30/06/2008 | <b>2. REPORT TYPE</b><br>Final Performance Report | <b>3. DATES COVERED (From - To)</b><br>Jan 2005 to April 2008 |
|--|---|---|

|   |  |
|---|--|
| <b>4. TITLE AND SUBTITLE</b><br><br>THE MOLECULAR DESIGN OF HIGH-PERFORMANCE CARBON MATERIALS | <b>5a. CONTRACT NUMBER</b><br>FA9550-05-1-0060 |
|   | <b>5b. GRANT NUMBER</b>                        |
|   | <b>5c. PROGRAM ELEMENT NUMBER</b>              |

|   |                             |
|---|-----------------------------|
| <b>6. AUTHOR(S)</b><br><br>Thies, Mark C. | <b>5d. PROJECT NUMBER</b>   |
|   | <b>5e. TASK NUMBER</b>      |
|   | <b>5f. WORK UNIT NUMBER</b> |

|  |   |
|--|---|
| <b>7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)</b><br><br>Clemson University<br>Dept. of Chemical Engineering<br>Clemson, SC 29634-0909 | <b>8. PERFORMING ORGANIZATION REPORT NUMBER</b> |
|--|---|

|  |   |
|--|---|
| <b>9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)</b><br>Dr. Charles Lee, AFOSR/NA<br>875 N. Randolph Street<br>Suite 325, Room 3112<br>Arlington, VA 22203 | <b>10. SPONSOR/MONITOR'S ACRONYM(S)</b>                                       |
|  | <b>11. SPONSOR/MONITOR'S REPORT NUMBER(S)</b><br><i>AFRL-SR-AR-TR-08-0574</i> |

**12. DISTRIBUTION / AVAILABILITY STATEMENT**  
Unclassified

**13. SUPPLEMENTARY NOTES**

**14. ABSTRACT**  
The separation of petroleum pitch into its oligomeric fractions via dense-gas extraction (DGE), followed by the application of both new and conventional analytical techniques to those fractions, has given us unique capabilities for identifying the specific molecular structures that exist in petroleum pitches. In particular, pitch fractions containing 98% monomer or 97% dimer were isolated by DGE and characterized using MALDI, MALDI-PSD, and FD mass spectrometry (MS); as well as by <sup>1</sup>H-NMR, UV-Vis, and FT-IR spectroscopy. Results indicate that the 98% monomer pitch fraction is approximately Gaussian with respect to molecular weight, with the dominant species present being methylated derivatives of the polycyclic aromatic hydrocarbons (PAH) benzofluorene (m/z = 216.4), chrysene, (m/z = 228.3), benzofluoranthene (m/z = 252.3), and their isomers. The distribution of the number of methyl substituents per molecule is also approximately Gaussian in nature, with a maximum at 2. Further, less than 10% of the alkyl substituents are ethyl. The overall mol wt distribution of the 97% dimer pitch fraction is also approximately Gaussian, and the most prevalent species (m/z = 454.6, 468.7, and 482.8) are consistent with condensation reactions of the most common monomer species with an accompanying loss of 4-6 hydrogens. Mesophase pitches that contain up to 25% dimer have been previously identified; thus, herein are proposed specific molecular structures that are significant constituents in mesophase pitch.

**15. SUBJECT TERMS**  
Carbon, carbon fiber, pitch, high-performance, high thermal conductivity, mesophase, molecular weight, oligomer, MALDI, mass spectrometry, mesophase, extraction, supercritical, fractionation.

|  |                         |                          |  |                                  |  |
|--|-------------------------|--------------------------|--|----------------------------------|--|
| <b>16. SECURITY CLASSIFICATION OF:</b> |                         |                          | <b>17. LIMITATION OF ABSTRACT</b><br>U U | <b>18. NUMBER OF PAGES</b><br>28 | <b>19a. NAME OF RESPONSIBLE PERSON</b><br>Thies, Mark C.           |
| <b>a. REPORT</b><br>U                  | <b>b. ABSTRACT</b><br>U | <b>c. THIS PAGE</b><br>U |  |                                  | <b>19b. TELEPHONE NUMBER (include area code)</b><br>(864) 656-5424 |

**THE MOLECULAR DESIGN OF HIGH-PERFORMANCE CARBON MATERIALS**

**CONTRACT NO. FA9550-05-1-0060**

**FINAL PERFORMANCE REPORT**

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# THE MOLECULAR DESIGN OF HIGH-PERFORMANCE CARBON MATERIALS

CONTRACT NO. FA9550-05-1-0060

## Executive Summary

As stated in the original proposal, submitted to AFOSR in May 2004, the objectives of this research project were to

1. Design and construct a dense-gas extraction (DGE) apparatus for the continuous fractionation of carbonaceous pitches.
2. Use the uniquely suitable process of DGE to produce oligomeric pitch cuts of narrow molecular weight distribution (MWD) for both analytical characterization and conversion into final carbon products.
3. Synthesize pure alkylated polycyclic aromatic hydrocarbons (PAHs) with molecular weights (mol wts) in the range of 300-2000. These unique compounds will serve as molecular calibration standards for our oligomeric pitch cuts, and will serve as important tools for establishing the response of matrix-assisted, laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) to alkylated PAH compounds.
4. With MALDI-TOF-MS (or MALDI for short) playing a key role, determine the absolute MWD and representative molecular structures of the oligomeric pitch cuts produced by DGE.

As discussed in the attached report, these objectives were largely accomplished, in spite of the originally requested budget being cut by almost 50%. Fortunately, about 1/3 of the budget shortfall was made up with an infusion of money from WP-AFRL during year 3 of the grant, and another 1/3 was made up by internal funds from our Center for Advanced Engineering Fibers and Films, an NSF Engineering Research Center.

With respect to Objective 1, both semibatch and continuous DGE apparatuses were designed and constructed for fractionating carbonaceous pitches (see Figs. 2 and 3). As proposed in Objective 2, narrow mol wt cuts of pitch were produced by DGE; Figs. 4a and 5a show mass spectra of pitch fractions consisting of 98% monomer and 97% dimer, respectively. Experimental details for carrying out the necessary fractionations are given in Tables 1-3.

Objective 3, the synthesis of pure PAHs and their use as calibration standards, had to be deleted from the project because of the budget cut. However, we were able to circumvent this problem to some extent by using the narrow mol wt pitch fractions themselves, which we were able to produce by semibatch DGE, as calibration standards. It was only because our DGE process worked so well in fractionating the feed pitch into its oligomeric constituents that this avenue was successful. The response of MALDI to monomer and dimer species in M-50 pitch is still work in progress, and future work would also be required to establish the response of MALDI to

the trimer and tetramer constituents of pitch, which are major constituents of mesophase, the precursor for high-performance carbon fibers.

Collaboration with Prof. Dr. Klaus Müllen's research group (and his mass spectrometry group leader Hans Joachim Räder) at the Max Planck Institute for Polymer Research (MPIP) in Mainz, Germany, was instrumental to our being able to accomplish Objective 4. Their group deserves much credit for realizing the significance of our being able to fractionate the starting raw pitch into its constituent oligomers: with these narrow mol wt cuts, we were in the unique position of being able to obtain truly quantitative molecular information on carbonaceous pitches.

Thus, in collaboration with MPIP, we applied a range of analytical techniques to our oligomeric cuts, including UV-Vis (Fig. 6), proton NMR (Fig. 7), and FT-IR (Fig. 8). By combining the characterization information obtained by the above techniques with mass spectrometry (MS), including field desorption MS (Fig. 10), MALDI-TOF-MS (Fig. 15), and MALDI-post source decay MS (Figs. 12-14), we were able to identify not just the "representative structures" that were the goal of Objective 4, but specific molecular structures for the monomer and dimer species that are significant constituents in both isotropic and mesophase pitches (see Figs. 11 and 15).

In conclusion, with the significant progress that was made during the course of this AFOSR grant, we are well-positioned towards achieving our long-term goals: (1) determining the structure-property relationships between carbonaceous pitches and the final, high-performance carbon product; and (2) designing and synthesizing pitches with the desired properties.

## **Supplementary Information for AFOSR Contract No. FA9550-05-1-0060**

### **A. Personnel Supported or Associated with Project**

|                         |  |
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| Ward M. Burgess         | PhD Student, Clemson University (expected grad. May 2009)  |
| Eduardo G. Cervo        | PhD Student, Clemson University (expected grad. Dec 2009)  |
| Sourabh U. Kulkarni     | PhD Student, Clemson University (expected grad. May 2010)  |
| Megan Owings            | Undergraduate (UG) Researcher, Clemson University. Senior Thesis Topic related to AFOSR grant, grad. May 2007. |
| Eric Davis              | UG Researcher, Clemson University, grad. May 2008.   |
| David Lehtihet          | UG Researcher, Clemson University  |
| Prof. Bahram Fathollahi | Associate Research Professor of Chemical Engineering, University of California at San Diego                    |
| Prof. Dr. Klaus Müllen  | Max Planck Institute for Polymer Research, Mainz, Germany  |
| Dr. Hans Joachim Räder  | Max Planck Institute for Polymer Research, Mainz, Germany  |

## **B. Refereed Journal Publications Acknowledging AFSOR Support**

Cervo, E. G.; Thies, M. C. Controlling the Oligomeric Composition of Carbon-Fiber Precursors by Dense-Gas Extraction. *J. Am. Ceram. Soc.* **2008**, *91*, 1416-1422.

Cervo, E. G.; Thies, M. C. Control of the Molecular Weight Distribution of Petroleum Pitches via Dense-Gas Extraction. *Chem. Eng. Tech.* **2007**, *30*, 742-748.

Cristadoro, A.; Kulkarni, S. U.; Burgess, W. A.; Cervo, E. G.; Räder, H. J.; Müllen, K.; Bruce, D. A.; Thies, M. C. Structural characterization of the oligomeric constituents of petroleum pitches, submitted for publication in *Carbon*, 2008.

The report beginning on the next page is essentially the same as the refereed publication recently submitted by our group under the auspices of AFOSR to the journal *Carbon*. Complete citation information on the paper is given above.

## Structural characterization of the oligomeric constituents of petroleum pitches

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### **Abstract**

The separation of petroleum pitch into its oligomeric fractions via dense-gas extraction (DGE), followed by the application of both new and conventional analytical techniques to those fractions, has given us unique capabilities for identifying the specific molecular structures that exist in petroleum pitches. Specifically, pitch fractions containing 98% monomer or 97% dimer were isolated by DGE and characterized using MALDI, MALDI-PSD, and FD mass spectrometry (MS); and <sup>1</sup>H-NMR, UV-Vis, and FT-IR spectroscopy. Results indicate that the 98% monomer pitch fraction is approximately Gaussian with respect to molecular weight, with the dominant species being methylated derivatives of the polycyclic aromatic hydrocarbons (PAH) benzofluorene (216.4 m/z), chrysene, (228.3 m/z), benzofluoranthene (252.3 m/z), and their isomers. The distribution of methyl substituents per molecule is also approximately Gaussian, with a maximum at 2. The molecular weight distribution of the 97% dimer pitch fraction is also approximately Gaussian, and the most prevalent species (m/z = 454.6, 468.7, and 482.8) are consistent with condensation reactions of the most common monomer species with an accompanying loss of 4-6 hydrogens. As mesophase pitches that contain up to 25% dimer were previously identified, herein are proposed specific molecular structures that are significant constituents in mesophase pitch.

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## 1. Introduction

Petroleum pitches are produced by the thermal polymerization of aromatic decant oil, a by-product of the fluid catalytic cracking (FCC) of the heavy gas oil fraction of crude oil, and are generally regarded to consist of oligomers of alkylated polycyclic aromatic hydrocarbons (PAHs), with the overall molecular weight (mol wt) ranging from approximately 200 to 2000 [1-2]. Such pitches can serve as raw materials for a wide range of carbon products, including carbon electrodes, carbon fibers for fuel cell substrates, high thermal conductivity carbon fibers, and the matrix phase of carbon-carbon composites [3-5]. Researchers have long recognized the important role that mol wt and structure play in the suitability of a given pitch for a particular application [1, 3, 5], but to date this understanding is primarily qualitative because of an inability to isolate and properly characterize the constituents of pitch.

A significant barrier to increased fundamental understanding of pitches has been the difficulty in separating them into narrow mol wt fractions that are more easily characterized and can serve as molecular calibration standards. The conventional technique for analytical-scale pitch separation, gel permeation chromatography (GPC), suffers from a number of disadvantages, including poor peak resolution and the incomplete solubility of higher mol wt pitches in even aggressive mobile-phase solvents [1,6-7]. Thies and co-workers [8-10] have recently developed a technique, known as dense-gas extraction (DGE), for separating pitches into fractions of relatively narrow mol wt. Such fractions can serve as standards for additional characterization work; in addition, we are investigating their large-scale production via DGE as “designer” pitches whose molecular compositions are tailored for a given, final carbon product application [11]. In this work, we report on the use of DGE to fractionate a commercially available petroleum pitch, M-50 pitch (Marathon Petroleum Company LLC), into its oligomeric constituents. Monomer-rich and dimer-rich cuts of the parent M-50 pitch were subsequently characterized in terms of both mol wt distribution and structure by a wide variety of analytical techniques, including field desorption mass spectrometry (FD-MS) and matrix-assisted, laser desorption/ionization, time-of-flight (MALDI-TOF) mass spectrometry, as well as <sup>1</sup>H-NMR, FT-IR, and UV-Vis spectroscopy. Taken together, this information was used to identify specific molecular structures that comprise petroleum pitches.

A unique feature of this study, in comparison to previous work, is the fractionation of petroleum pitch into its constituent oligomers. Only in recent years have researchers [11-12] developed the ability to monitor the molecular weight distribution (MWD) of a given pitch separation process via MALDI. Thus, DGE conditions were manipulated until monomer- and dimer-rich cuts of the desired purity were obtained.

One of the earliest studies on the fractionation and characterization of petroleum pitches was by Dickinson [13]. Fractions of Ashland A-240 pitch were produced by conventional solvent extraction and analyzed by NMR spectroscopy and vapor pressure osmometry (VPO). This information was used in conjunction with elemental analysis to propose average molecular structures for each isolated fraction. However, the MWD of these fractions was not determined. Kershaw and Black [14] performed work similar to that of Dickinson on both petroleum and coal-tar pitches; Electron Ionization (EI) MS was also applied to CCl<sub>4</sub>- and cyclohexane-soluble fractions of coal-tar pitch. Hutchenson et al. [15] used single-stage supercritical extraction with

toluene at 400 °C and pressures from 46 to 76 bar to separate Ashland A-240 pitch (a similar product to M-50) into light and heavy cuts. An average molecular structure was proposed for each fraction. However, GPC results indicated that all fractions obtained were relatively broad in mol wt, with monomer and dimer species being present in all samples in significant amounts. Kandiyoti and co-workers, one of the leading groups in the analytical characterization of heavy fossil fuels, have recently published a comprehensive review paper [16]. However, their work is focused on the characterization of coal-tar pitches and asphaltenes, neither of which exhibit the oligomeric nature of petroleum pitches.

## 2. Experimental

### 2.1 Materials

The feed pitch to the DGE process was an isotropic pitch, M-50, which was obtained from Marathon Petroleum Company LLC. The mass spectrum of M-50, as obtained by MALDI, is shown in Fig. 1. The oligomeric nature of the pitch is obvious. Of course, the oligomers themselves are not pure, as the starting “monomer” for the pitch (i.e., the aromatic decant oil), is itself a polydisperse material. What we have labeled “monomer” has a mol wt range of 210-388, roughly centered about a maximum of 280; “dimer” 388-645, centered about 470; trimer 645-890, centered about 730; and tetramer 890-1120, centered about 990. As described in the Results and Discussion section, four fractions of M-50 pitch were isolated by DGE and then subjected to analysis: fractions containing 79 and 98% monomer, and fractions consisting of 89 and 97% dimer. The stated purities were based on MALDI analysis, assuming that species intensity is proportional to species mole number [12, 17].

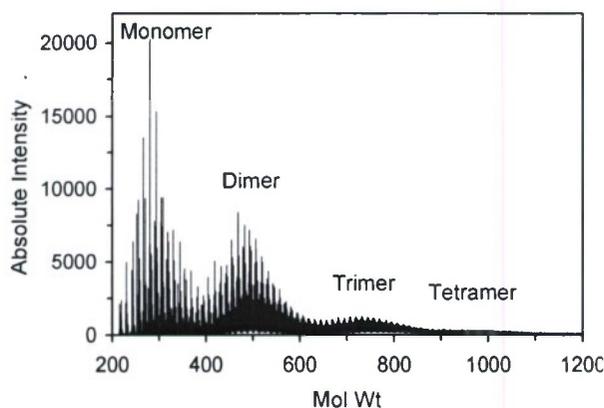


Fig. 1 – MALDI mass spectrum of M-50 petroleum pitch.

Both toluene (HPLC grade, 99.8% purity, CAS 108-88-3) and methanol (HPLC grade, 99.9% purity, CAS 67-56-1) were obtained from Fisher Scientific and were used as dense-gas solvents without further purification.

## 2.2 Dense-gas extraction apparatus and procedure

Because DGE is reported in detail elsewhere [10, 12], only a brief description is given here. The two monomer-rich pitch fractions (PFs) were produced by continuous DGE (see Fig. 2); the two dimer-rich PFs by semi-batch DGE (Fig. 3).

The continuous DGE unit consists of a packed column with a height of 1.5 m of packing and an inner diameter of 1.8 cm. For a typical experiment, molten M-50 pitch is fed to the top of the column at ~120 g/h via a single-screw extruder, and a liquid chromatography pump is used to deliver the dense-gas solvent at ~600 g/h to the bottom of the column. The dense-gas solvent flows up the column, the pitch feed flows down the column, and selected fractions of the feed pitch are extracted into the solvent phase. As would be expected, higher operating pressures increase the density of the solvent and increase the average mol wt of the overhead extract. However, column operating temperature has been found to exhibit more complex behavior, with the establishment of a positive temperature gradient from the bottom to the top of the column yielding the best product purities [11]. A liquid-level detector at the bottom of the column operates based on the difference in electrical resistivity between the top and bottom phases and ensures complete separation between the solvent-rich top phase and pitch-rich bottom phase. Steady-state operation is typically reached within an hour, and an experimental run takes 6-12 h, depending on how much pitch fraction is to be produced.

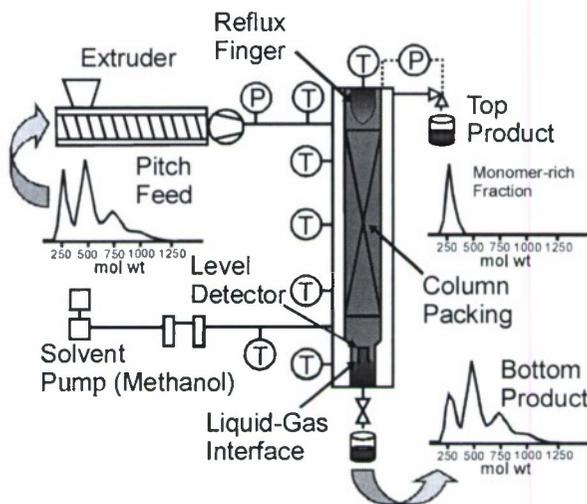
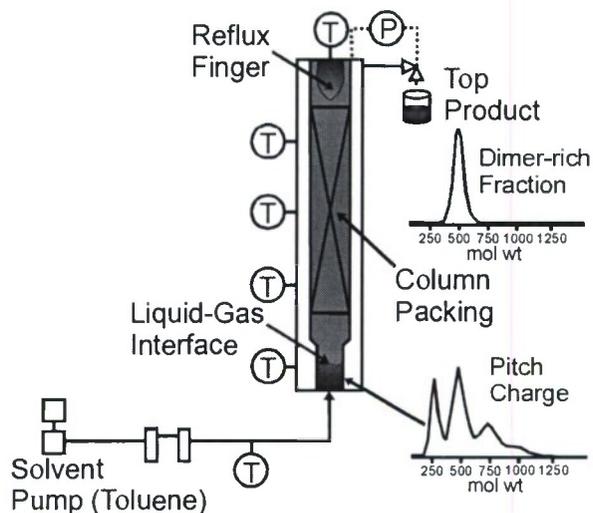


Fig. 2 – DGE apparatus for continuous fractionation of pitches.



**Fig. 3 – DGE apparatus for semi-batch fractionation of pitches.**

For a semi-batch run (see Fig. 3), ~15 g of the M-50 feed pitch is charged to a stillpot in the bottom of a packed column similar to that described above. Continuous flow of the dense-gas solvent is then initiated. The solvent flows through the pitch charge, extracts a portion of the pitch depending on the operating (column) temperature and pressure, flows up the column, and removes the extracted pitch fraction out as top product. As with continuous DGE, a positive temperature gradient is established along the length of the column to enhance product purity. Liquid reflux of a portion of the product back down the column, which is created by use of a heated reflux finger, is also used to enhance overhead product purity.

### **2.3 Analytical characterization of pitch fractions isolated by DGE**

Pitch fractions isolated by the DGE experiments described above were subjected to a wide range of analytical characterization techniques, as described below. Field desorption–mass spectrometry (FD-MS) analyses were performed using a Fisons Instruments VG ZAB2\_SE\_FPD Sectorfield mass spectrometer.  $\text{CH}_2\text{Cl}_2$  (Fisher Scientific, HPLC grade, CAS 75-09-2) was used as the solvent for all analyzed pitch fractions, and a drop of the resulting solution was placed on the emitter of the mass spectrometer. Ions were produced by field desorption of the analytes by employing an extraction potential of 8 kV. Calibration was carried out before each measurement by using acetone (Fluka, 99.5%, CAS 67-64-1).

$^1\text{H-NMR}$  analyses were performed with a Bruker 700 MHz NMR Spectrometer Avance instrument. Five mg of a given pitch fraction were dissolved in deuterated 1,2-dichlorobenzene- $d_4$  (Deutero GmbH, 99%, CAS 2199-69-1), and measurements were carried out at 80°C. This above-ambient temperature was used to improve resolution and to ensure that all fractions were completely soluble in the NMR solvent.

UV-Vis analyses were carried out with a Perkin Elmer Lambda 9 instrument, with all pitch fractions being dissolved in 1,2,4 trichlorobenzene (Sigma-Aldrich, 99%, CAS 120-82-1). FT-IR analyses of the monomer-rich PFs were performed on the bulk analyte with a Nicolet 730 spectrometer.

Elemental analysis was performed with a PerkinElmer CHNS/O Model 2400 Series II elemental analyzer.

#### ***2.4 MALDI and post-source decay***

For MALDI analyses, samples were analyzed using a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer equipped with 337 nm nitrogen laser. The reflectron mode was used for this study. The target plate was positively charged and set to 19.0 kV; the secondary ion source to 16.5 kV, the lens to 9.40 kV, and the reflector to 20 kV. Ions generated after laser bombardment were accelerated using pulsed-ion extraction after a time delay of 90 ns. Other important parameters used during analyses included: a detector gain of 4.0, a resolution of 2.0, and a mol wt suppression up to 210. MALDI calibration was carried out using a fullerite mixture (Sigma-Aldrich, CAS 131159-39-2) before the analysis. Laser powers ranging from 20 to 26% of maximum were used for the MALDI analysis of M-50 petroleum pitch and its fractions, with 200 laser shots being used to generate the spectra shown herein. MALDI m/z were accurate to within  $\pm 0.1$  Da.

Both solid-state and solvent-based sample preparation methods were used to prepare samples for MALDI analysis. Based on previous studies from our groups [2, 18], 7,7,8,8-tetracyanoquinodimethane (TCNQ; 98% min. from TCI America, CAS 1518-16-7) was used as the matrix. For the solid-state analysis of M-50 pitch, the pitch and TCNQ were mixed using a grinding mill (Thermo Electron Corp., model Wig-L-Bug). The sample was then transferred to the MALDI target-plate cell using our water-spotting method [2, 8]. For the solvent-based sample preparation of monomer-rich and dimer-rich fractions, a fine powder of TCNQ was prepared using a grinding mill. A thin film of this matrix powder was then transferred to the MALDI target via water-spotting. Each pitch fraction was then dissolved in carbon disulfide (Fisher Scientific; 99.9% min purity, CAS 75-15-0) at a concentration of 0.02 w/v %, and a drop of the prepared solution was placed on the film of TCNQ and allowed to dry before analysis.

Post-source decay (PSD) analyses were performed with the MALDI instrument described above, operating in the reflectron mode and with the Bradbury-Nielsen ion gate activated. Solvent-based sample preparation was used as described above, with 1,2,4 trichlorobenzene (VWR, GPC grade; 99% min. purity, CAS 120-82-1) being used to dissolve the samples at a w/v % of 0.1. The ion gate was programmed to pass parent species ions of specified mol wt to within  $\pm 5$  Da, as well as all fragment ions associated with the parent species. The target plate was positively charged and set to 19.0 kV, the secondary ion source to 16.8 kV, and the lens to 7.6 kV. Reflector voltage was initially set to 20 kV and then progressively reduced to analyze fragment ions of decreasing mol wt. The pulsed ion extraction delay was set to 90 ns, the resolution to 1.0, and 300 laser shots were used to generate all spectra. The laser power ranged from 26 to 33%, with higher laser power than that employed in conventional MALDI being required to increase the fragmentation of a given pitch species. The detector gain employed ranged from 6

to 16, with higher gains required to achieve an adequate detector response for smaller ion fragments. Fragmentation spectra via PSD are less accurate than conventional MALDI, that is, to within  $\pm 0.25$  Da.

### 3. Results and Discussion

#### 3.1 Dense-gas extraction

Results of the DGE experiments are summarized in Tables 1-3. In Table 1, operating conditions and results are shown for two experiments with continuous DGE (Fig. 2), in which monomer-rich overhead PFs were obtained. Methanol, with a critical temperature ( $T_c$ ) and pressure ( $P_c$ ) of 239.5 °C and 81.0 bar, was used as the dense-gas solvent for the first fractionation; toluene ( $T_c = 318.6$  °C,  $P_c = 41.1$  bar) was used for the second. In both cases, a positive temperature gradient was established across the DGE column, with the bottom at 330, the middle at 350, and the top at 380 °C. The exiting flow rate of the top phase was  $\sim 15$  g/h on a solvent-free basis, with the solvent-rich top phase containing 2.7-2.8 wt % pitch. MALDI spectra for the 98% monomer and 79% monomer pitch fractions (PFs) are shown in Fig. 4; clearly, methanol is more selective for monomer than toluene.

Experimental details for the two semi-batch runs (Fig. 3) are given in Tables 2 and 3. In both cases, toluene was used as the dense-gas solvent, the solvent feed flow rate was 600 g/h, the same positive temperature gradient was used as for the continuous DGE runs described above, and the reflux finger was maintained at 380 °C. Operating pressures, collection times, and the amount of pitch collected as overhead product on a solvent-free basis are shown for selected pitch fractions, with the last fractions having the desired dimer purity. MALDI spectra for the 89 and 97% dimer PFs are shown as Fig. 5. Comparing Tables 2 and 3, we see that the key to obtaining the 97% dimer PF was to simply extend the run time of the 89% dimer experiment until the desired higher purity was achieved.

#### 3.2 Analytical and structural characterization of monomer-rich pitch fractions

The results from a variety of analytical methods were collectively used to develop a series of likely compounds that are present in monomer and dimer PFs. These efforts first used the results from mass spectral experiments to arrive at a likely composition for a given species. The MALDI-PSD fragmentation pattern in conjunction with proton NMR data helped to establish the presence, nature, and location of any alkyl side groups on the aromatic ring structures. Finally, UV-Vis and FTIR data were used to eliminate certain isomers whose absorption characteristics do not match the observed spectra.

**Table 1 - Continuous DGE experiments for collection of monomer-rich overhead pitch fraction.**

| Dense-Gas Solvent | Pitch Feed (g/h) | Solvent Feed(g/h) | Pressure (bar) | Overhead Pitch (g/h) | $\bar{M}_n$ | % Monomer |
|-------------------|------------------|-------------------|----------------|----------------------|-------------|-----------|
| Methanol          | 120              | 540               | 36             | 15.0                 | 287         | 98        |
| Toluene           | 120              | 600               | 42             | 15.5                 | 331         | 79        |

**Table 2 - Semi-Batch DGE experiment for collection of 89% dimer overhead pitch fraction.**

| Fraction No. <sup>b</sup> | Pressure (bar) | Collection Time (min) | Dry Mass (g) | $\bar{M}_n$ | % Dimer |
|---------------------------|----------------|-----------------------|--------------|-------------|---------|
| M-50 Pitch <sup>a</sup>   | -              | -                     | 16.05        | 536         | 45      |
| 2                         | 29             | 60                    | 0.85         | 361         | 11      |
| 4                         | 36             | 60                    | 0.69         | 375         | 37      |
| 7                         | 42             | 30                    | 0.33         | 437         | 73      |
| 10                        | 46             | 30                    | 0.31         | 458         | 89      |

<sup>a</sup> Feed to semi-batch DGE column.

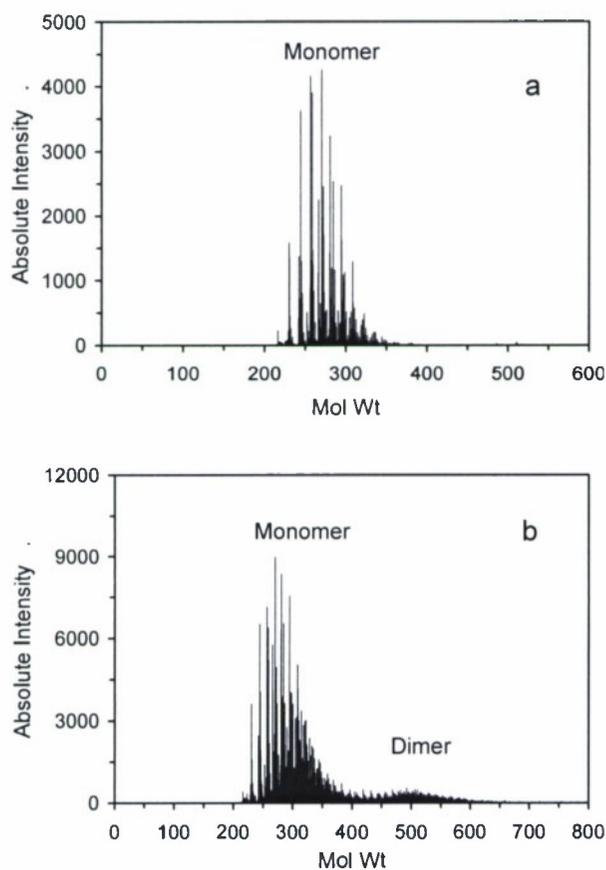
<sup>b</sup> Selected fractions are shown for illustrative purposes.

**Table 3 - Semi-batch DGE experiment for collection of 97% dimer overhead pitch fraction.**

| Fraction No. <sup>b</sup> | Pressure (bar) | Collection Time (min) | Dry Mass (g) | $\bar{M}_n$ | % Dimer |
|---------------------------|----------------|-----------------------|--------------|-------------|---------|
| M-50 Pitch <sup>a</sup>   |                |                       | 15.76        | 536         | 45      |
| 1                         | 29             | 60                    | 2.99         | 328         | 17      |
| 4                         | 36             | 60                    | 0.90         | 392         | 33      |
| 7                         | 42             | 30                    | 0.55         | 442         | 62      |
| 11                        | 46             | 30                    | 0.32         | 490         | 90      |
| 13                        | 46             | 40                    | 0.15         | 495         | 97      |
| 17                        | 49             | 40                    | 0.10         | 514         | 97      |

<sup>a</sup> Feed to semi-batch DGE column.

<sup>b</sup> Selected fractions are shown for illustrative purposes.

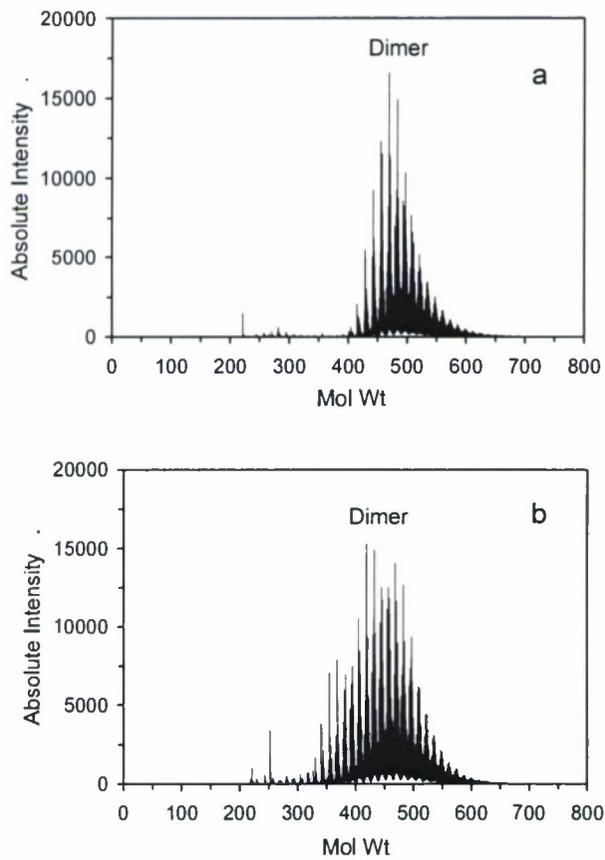


**Fig. 4 – MALDI mass spectra of (a) 98% monomer and (b) 79% monomer fractions isolated from M-50 pitch.**

### 3.2.1 UV-Vis

All PAH structures proposed in this investigation for the monomer-rich PF of M-50 pitch were selected, from among other possible isomers, by considering their UV-Vis absorption spectra and comparing with the absorption spectra for the 79 and 98% monomer PFs. As shown in Fig. 6, species present in the 98% monomer PF absorb strongly between 300 and 360 nm and weakly at higher wavelengths. Further, mass spectral data (discussed later) indicate that a component of the 98% monomer PF leads to an MS signal with an  $m/z$  of 216.4. A known PAH with this molecular weight is benzo[fluorene], but there are several isomers of this compound. Therefore, UV-Vis absorption data was used to predict which isomers are present within the pitch sample. For example, it is known that benzo[b]fluorene exhibits absorption behavior similar to that of the pitch sample [19]; thus, it is likely that it is a significant constituent in the 98% pure monomer. On the other hand, the PAH molecule benzo[a]pyrene absorbs strongly from 350 to 410 nm [19], and thus, would not be expected to be a major constituent in the 98% monomer PF. The monomer fraction of 79% purity absorbs light at higher wavelengths (red shift) in comparison to

the 98% monomer PF. This is probably due to the presence of species with a larger polycyclic system, evidence that is consistent with the broader signal distribution of this monomer fraction in the FD mass spectrum (see below). Additional information on the use of UV-Vis to assist in the selection of the most likely PAH structures is given in the subsequent discussions below.

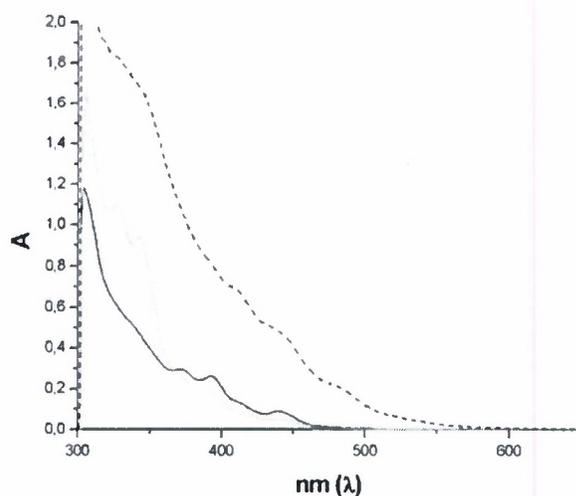


**Fig. 5 – MALDI mass spectra of (a) 97% dimer and (b) 89% dimer fractions isolated from M-50 pitch.**

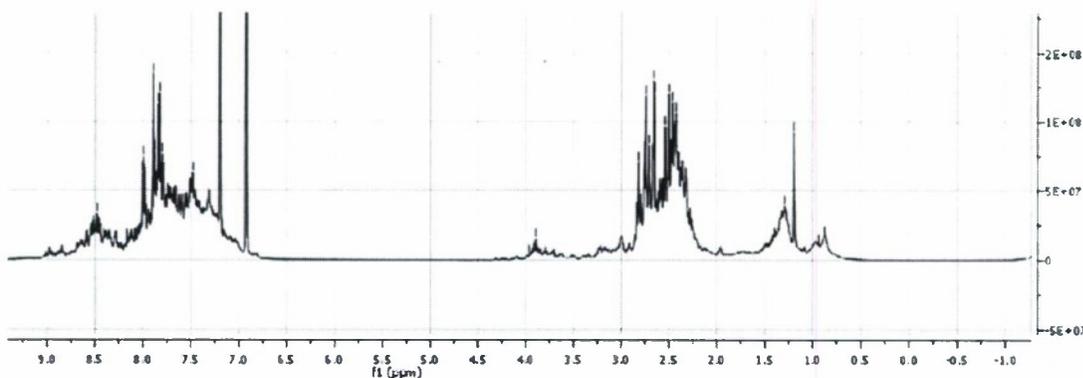
### 3.2.2 Proton NMR spectroscopy

$^1\text{H}$ -NMR analyses of the 98% monomer PF is given in Fig. 7. The protons with NMR chemical shifts between 2.76 and 2.43 ppm are related to the presence of  $-\text{CH}_2\text{-R}$  ( $\text{R} = \text{alkyl or H}$ ) groups attached to the aromatic rings, whereas the species with chemical shifts between 8.85 and 7.30 ppm are attributable to protons directly bonded to aromatic carbons. The ratio between aliphatic hydrogens in the  $\alpha$  position relative to the aromatic rings vs. aromatic protons was evaluated via integration of the corresponding NMR signals and found to be 1/1.33. The strong signals at 7.20 and 6.94 ppm arise from the *o*-dichlorobenzene solvent and at 1.20 ppm from trace amounts of water. The presence of alkyl substituents with propyl or longer chains is recognized by the peaks between 0.94 and 0.88 ppm, which are related to aliphatic protons ( $\phi\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-}$ ) in the  $\beta$

position with respect to an aryl-aliphatic group, and by the signals between 1.26 and 1.40 ppm, which are related to aliphatic protons ( $\phi$ -CH<sub>2</sub>-CH<sub>2</sub>-) in the  $\alpha$  position with respect to a aryl-aliphatic group. They are, however, relatively rare when compared to the number of methyl groups directly connected to the aromatic core (related to the signal between 2.76 and 2.43 ppm). From the NMR spectrum, the ratio CH<sub>3</sub>-CH<sub>2</sub>- $\phi$ /CH<sub>3</sub>- $\phi$  is calculated to be 1/15. The peak at 3.96 ppm is related to the presence of sp<sup>3</sup> hybridization that bridges two aromatic rings, evidence of the presence of a methylene bridge between two aromatic rings.



**Fig. 6 – UV-Vis spectra for the 79% (gray) and 98% (black) monomer fractions, and for the 97% dimer fraction (dotted line) of M-50 pitch.**

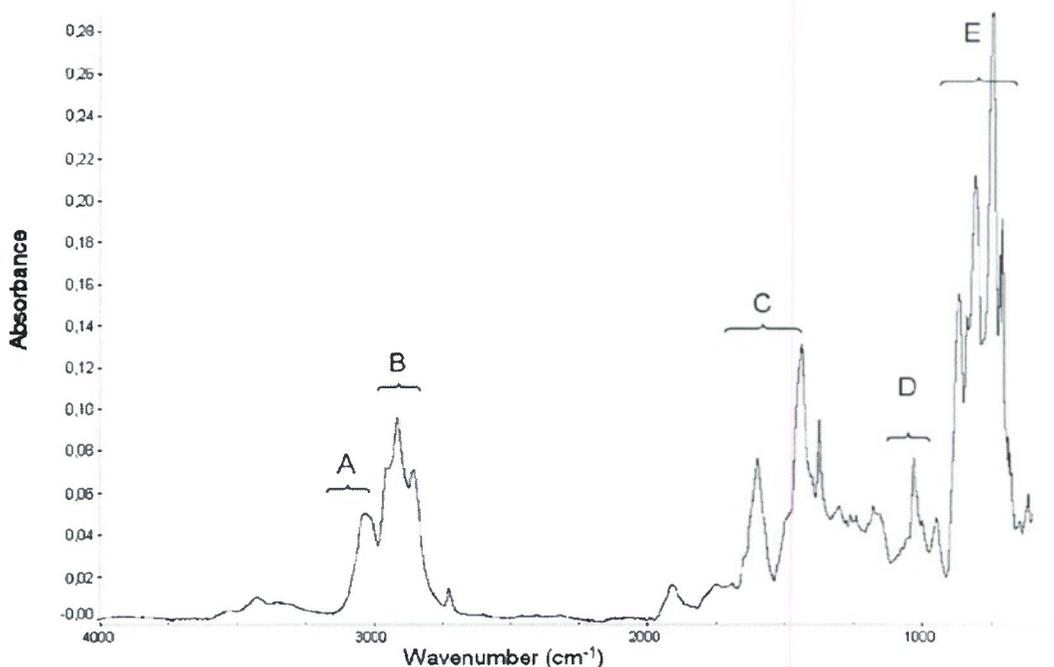


**Fig. 7 – <sup>1</sup>H-NMR of the 98% monomer fraction of M-50 pitch.**

### 3.2.3 FT-IR spectroscopy

The FT-IR absorption spectrum for the 98% monomer PF is shown in Fig. 8. The band A at 3046-3014  $\text{cm}^{-1}$  of weak intensity is related to aromatic C-H stretching. The bands at 2961, 2915, and 2856  $\text{cm}^{-1}$  of the group B can be related to stretching of the methylic C-H and provides evidence for the presence of saturated  $\text{sp}^3$  carbon atoms. The group C bands at 1598 and 1438  $\text{cm}^{-1}$  are caused by stretching of the C=C atoms of the aromatic ring, the group D bands are related to the aryl C-H in-plane bending, and the group E bands are related to out-of-plane bending of aryl C-H groups.

Note that group E consists of three bands. For PAHs, these bands can be related to the number of neighboring hydrogen atoms present on aromatic rings [20]. Taking as a model system



**Fig. 8 – FT-IR spectrum for the 98% monomer PF. The spectrum for the 79% monomer PF is very similar to that shown above.**

methyl-substituted benzo[b]fluorene (see Fig. 9), the FT-IR spectrum will show three absorption bands: one for the isolated hydrogen on Ring 1, one for the two neighboring H atoms on Ring 1, and one for the two hydrogen atoms on Ring 2. However, only two bands would be present for  $\alpha$ -substituted benzo[b]fluorene. Thus, the presence of three absorption bands provides evidence that alkylation of the PAH aromatic backbone in the monomer-rich fraction occurs preferentially at the  $\beta$  position.

### 3.2.4 FD, MALDI, and MALDI-PSD mass spectrometry

FD-MS spectra for the 98% and 79% monomer PFs are shown in Figs. 10a and b. FD-MS was used in addition to MALDI, as the matrix (i.e., TCNQ) signal at 204  $m/z$  could have interfered with the signals for low mol wt pitch species. However, this did not turn out to be the case, as spectra obtained by the two different MS techniques were, in fact, found to be essentially identical. Our analysis of the monomer-rich PFs, based on information obtained from FD, MALDI, and MALDI-PSD mass spectrometry, is summarized in Table 4.

The lowest-mass signal present in the FD spectrum (Figs. 10a and b, blue rectangle) of the monomer PF at  $m/z$  216.4 is due to the presence of the PAH benzofluorene (mol wt = 216.3) and its isomers, such as benzo[b]fluorene (see Fig. 11a). The NMR spectra in Fig. 7 indicates that benzo[c]fluorene is also equally probable, but not benzo[a]fluorene. Rectangular blue marks delineate a signal distribution that starts at 216.4, has a repeating unit of 14 Da, and extends to 300.8 Da. This distribution provides strong evidence for the presence of alkyl groups anchored to the base aromatic structure of benzofluorene (see Table 4 and Fig. 11 b).

The fragmentation behavior via MALDI-PSD of the “blue rectangle” signal distribution described above is given in Fig. 12. The spectra at  $m/z = 216.3$  (Fig. 12a) is consistent with the benzofluorene structure in two ways: (1) No significant fragments are observed, which is consistent with mass spectra for the fluorenes [21], and (2) the low-intensity peak at 202.5  $m/z$  is consistent with the loss of the methylene group from benzofluorene. Fragmentation patterns are shown in Figs. 12b-e for the “blue rectangle” signal distribution that includes species with an  $m/z = 230.4, 244.3, 258.4,$  and  $272.5$ . In every case, a de-methylated ion (i.e., ~15 Da less than the parent ion) of appreciable magnitude is present. Furthermore, the stability of the de-methylated benzofluorene ion is consistent with the mass spectrum for the methylfluorenes, which also have a highly stable de-methylated ion [21]. For the species at 272.5 (Fig. 12e), a de-ethylated ion at

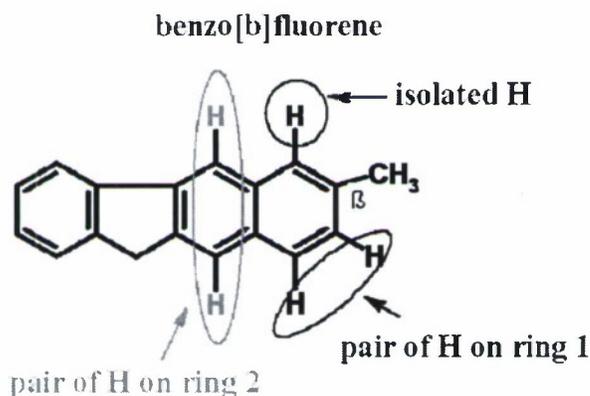


Fig. 9 – FT-IR spectra for the monomer-rich PF indicates that methyl substitution of the PAHs preferentially occurs at the  $\beta$  position.

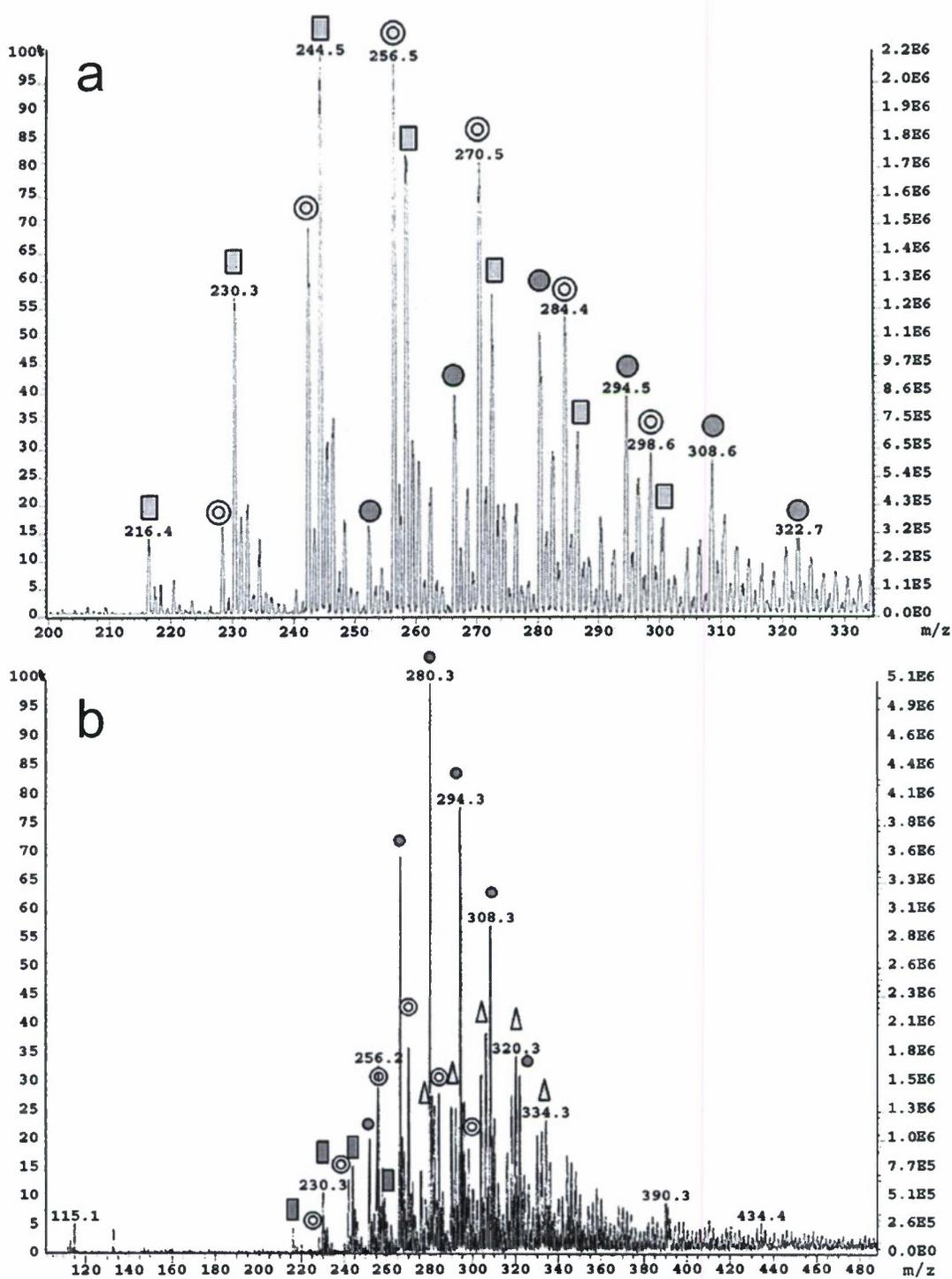


Fig. 10 – FD mass spectra of pitch fractions with purities of (a) 98 and (b) 79% monomer.

**Table 4 – Molecular weights and degree of alkylation of species present in the monomer-rich fraction of M-50 pitch as determined by FD-MS and MALDI-PSD-MS.**

|     | Blue rectangles    | Yellow rings       | Orange dots        | Green triangles <sup>a</sup> | Alkyl substituents  |
|-----|--------------------|--------------------|--------------------|------------------------------|---|
| m/z | 216.4              | 228.3              | 252.3              | 278.3                        | 0   |
| m/z | 230.3              | 242.4              | 266.5              | 292.2                        | CH <sub>3</sub>   |
| m/z | 244.5 <sup>b</sup> | 256.5 <sup>b</sup> | 280.5 <sup>b</sup> | 306.3 <sup>b</sup>           | 2 x CH <sub>3</sub>   |
| m/z | 258.4              | 270.5              | 294.5              | 320.3                        | 3 x CH <sub>3</sub>   |
| m/z | 272.6 <sup>c</sup> | 284.4              | 308.6              | 334.5                        | 4 x CH <sub>3</sub> or (CH <sub>2</sub> CH <sub>3</sub> + 2 x CH <sub>3</sub> ) |
| m/z | 286.7 <sup>c</sup> | 298.6              | 322.7              |                              | 5 x CH <sub>3</sub> or different combinations of methyl, ethyl groups.          |
| m/z | 300.8 <sup>c</sup> |                    |                    |                              | 6 x CH <sub>3</sub> or different combinations of methyl, ethyl groups.          |

<sup>a</sup> This PAH series was not observed in appreciable amounts in the 98% monomer PF.

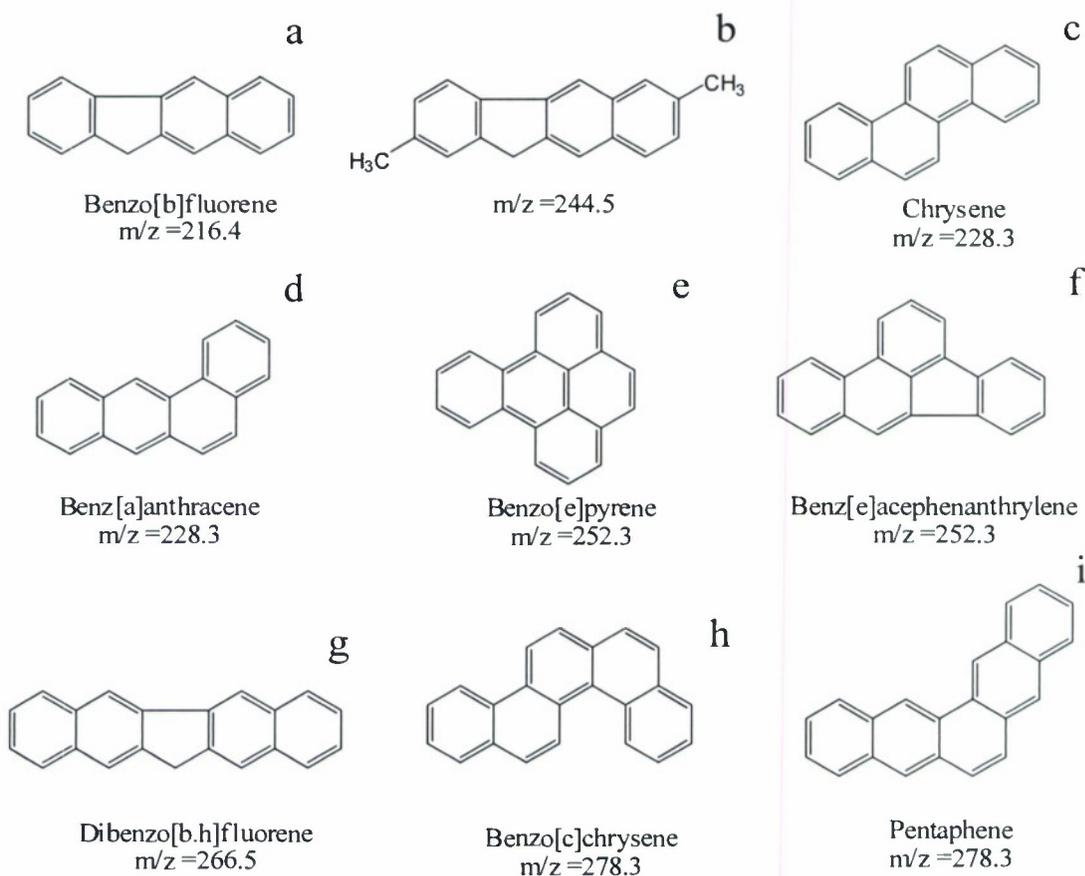
<sup>b</sup> The most prevalent species in each PAH distribution. (all contained two methyl substituents)

<sup>c</sup> These signals were not prevalent in the 79% monomer PF.

243.6 is observed at less than one-tenth the intensity of the de-methylated ion at 257.3. Loss of a methyl group from an ethyl (vs. a methyl) substituent is also possible for the species with m/z of 244.3 and 258.4, but is unlikely based on the relatively rare occurrence of ethyl groups in our monomer-rich PFs, as indicated by <sup>1</sup>H-NMR. PSD could not be applied to the higher mol wts in the benzofluorene series because of the difficulty in isolating the species of interest from nearby signals of comparable intensity.

In Fig. 10, another PAH and its alkylated homologs are shown by the signal distribution labeled with yellow rings and begin with an m/z of 228.3, with this signal being due to the presence of chrysene and related isomers (Figs. 11c-d). UV-Vis of the monomer fraction eliminates the linear naphthacene as a significant species having an m/z of 228.3. As was the case for benzofluorene, the distribution has a repeating unit of 14 Da, indicating the addition of alkyl groups up to an m/z of 298.6 (see Table 4). Once again, the most prevalent structure has the equivalent of two methyl groups (m/z = 256.5).

PSD was not carried out on the species at 228.3, 242.4, or 284.4 Da because of the difficulty in isolating these signals from those nearby. As for the benzofluorene series described above, fragmentation spectra for the species at 256.2 and 270.2 m/z (see Figs. 13a-b) indicate the predominance of methyl substituents. A signal for de-ethylated ions is observed only for the higher mol wt species, here for m/z = 298.5, see Fig. 13c. A signal (albeit a very low intensity one) for loss of yet another methyl group is also observed at an m/z of 254.7.



**Fig. 11 – PAH structures present in the 98% monomer PF: (a) Benzo[b]fluorene ( $m/z = 216.4$ ) and (b) its most common alkylated homolog ( $m/z = 244.5$ ). PAH structures for the  $m/z = 228.3$  series include (c) chrysene, (d) benz[a]anthracene, and their alkylated homologs; and for the 252.3 series include (e) benzo[e]pyrene, (f) benz[e]acephenanthrylene, and their alkylated homologs. Isomers of dibenzofluorene (g), and alkylated homologs thereof, may also be present. For the 278.3 series, the PAH structures present would include (h) benzo[c]chrysene, (i) pentaphene, their isomers, and alkylated homologs thereof.**

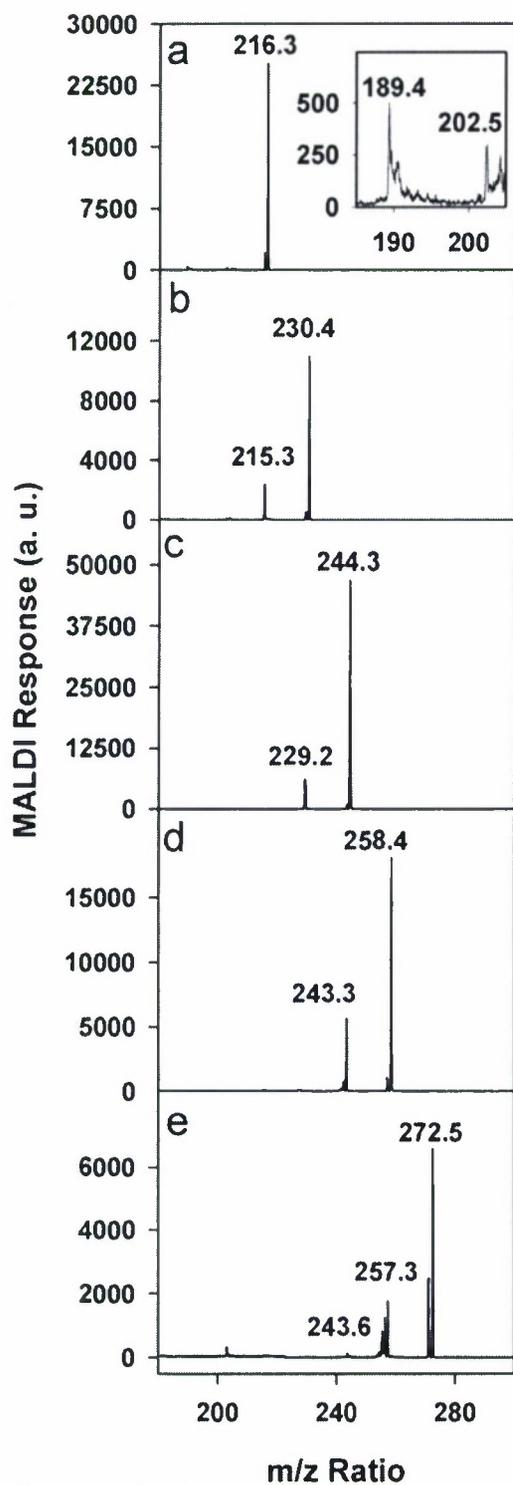


Fig. 12 – PSD results for the series of PAHs beginning at benzo[fluorene] ( $m/z = 216.3$ ): (a) base aromatic structure; (b-d) one to three methyl substituents, respectively; (e) limited ethyl substituents are also likely to be present.

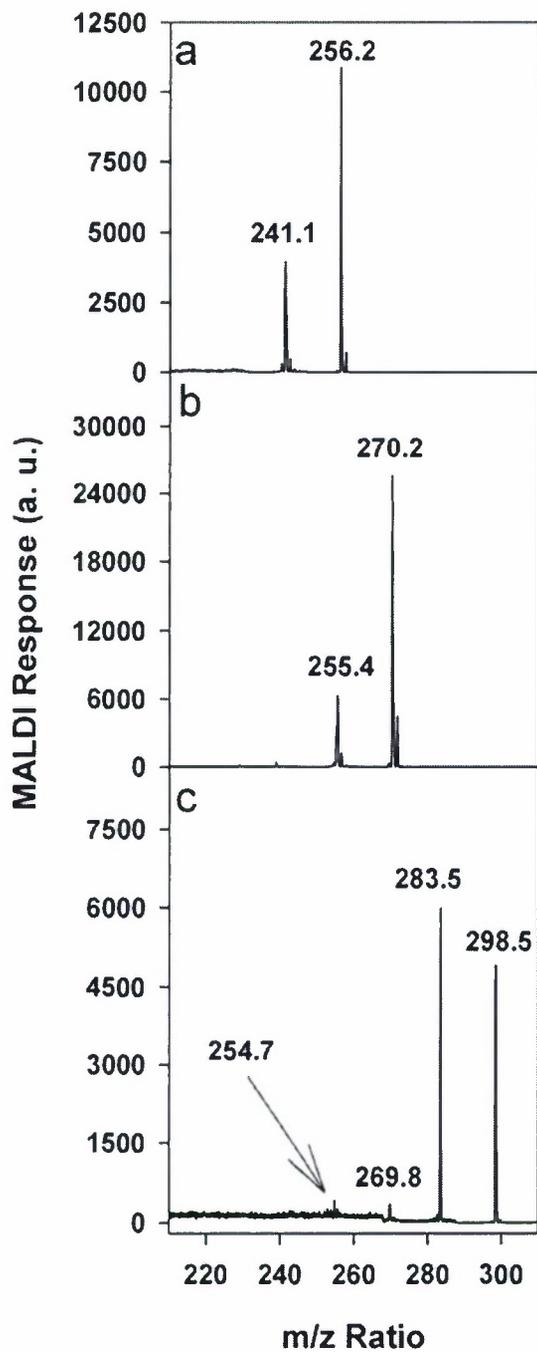


Fig. 13 – PSD results for the series of PAHs beginning with chrysene and benz[a]anthracene ( $m/z = 228.3$ ): (a-b) two and three methyl substituents, respectively; (c) limited ethyl substituents are also likely to be present.

The next series of PAHs begins with the signal at 252.4 m/z (Fig. 10, orange dots) and includes 5-ringed compounds, such as the isomers of benzofluoranthene and also benzo[e]pyrene (Figs. 11e-f), with the UV-Vis spectra of the above compounds being consistent with that observed for the pitch fractions. As with the previous two series of PAH compounds, a distribution of signals differing from one another by multiples of 14 is observed. PSD results for m/z = 266.5 (see Fig. 14b) show no de-methylation peaks, but this is not surprising, as mass spectra for methylated fluoranthene and pyrene show essentially no tendency for loss of a single methyl ion [22,23]. On the other hand, for all species with an m/z above 266.5, including 280.4, 294.3, and 308.5 (Figs. 14c-e, respectively), the loss of methyl ions was observed, and for the 308.5 m/z species, a signal for a de-ethylated ion is also present. Another PAH series that cannot be ruled out would be isomers of dibenzofluorene, with the base aromatic having an m/z = 266.5 (see Fig. 11g).

All PAH series discussed up to now were prominent in pitch fractions that contained either 79% or 98% monomer. However, the PAH series beginning with the species having an m/z of 278.3 (green triangles, Fig. 10b) is essentially absent in the pitch fraction containing 98% monomer, demonstrating how DGE operating conditions can be used to control the composition of pitch fractions. Typical 5-ring PAHs that would be expected in the 278.3 series are given as Figs. 11h,i. As shown in Table 4, the alkylated homologs of the 278.3 series extend up to 334.5 m/z, which would result from the addition of 4 methyl (less likely would be an ethyl and 2 methyl) groups. Signal intensities for species in the 278.3 series were not strong enough to carry out PSD, so we were not able to confirm that all multiples of 14 in the series, are, in fact, the result of alkylation. Nevertheless, this was the case for the other three PAH series that were studied, so one would expect the trend to continue.

### *3.3 Analytical and structural characterization of dimer-rich pitch fractions*

The MALDI mass spectrum for the 97% dimer PF is given in Fig. 15. FD-MS was also applied to this pitch fraction, and the resulting spectrum (not shown) was found to be very similar to what was obtained via MALDI.

The molecular structures of the most prevalent dimer species in the 97% dimer PF were predicted by assuming condensation reactions, with the accompanying loss of hydrogen atoms, between the most prevalent monomer species in the 98% monomer PF (see Fig. 10). Results of this exercise are given in Table 5, with examples of the resultant dimer structures given in Fig. 16. Comparison of these results with the MALDI-MS spectrum in Fig. 15 for the dimer PF reveals several interesting points: (1) Condensation reactions, with the elimination of 4-6 hydrogen atoms, were successful in predicting the origin of the most prevalent dimer species. (2) The geometry of the monomer “reactants” is such that the formation of dimers from the loss of larger amounts of hydrogen (e.g., 8-10 atoms) would be unlikely. Consistent with this observation is the fact that assuming the loss of larger amounts of hydrogen from condensation of the most prevalent monomer species did not produce the major dimer species observed in the spectrum. (3) The benzofluorene (m/z = 216.3) monomer seems to have participated in the formation of dimer more than can be explained by its concentration in Fig. 10a. Another possible explanation is that the distribution of monomeric species in the pitch is no longer similar to what it was in the pitch precursor because of the different reactivities of the various

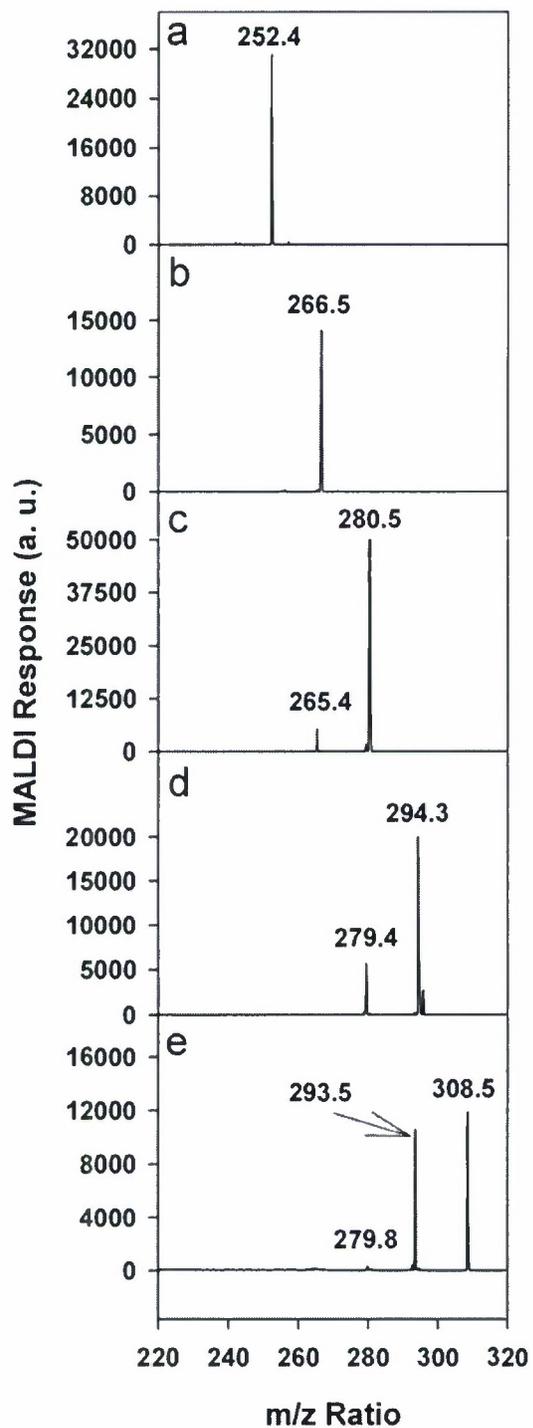
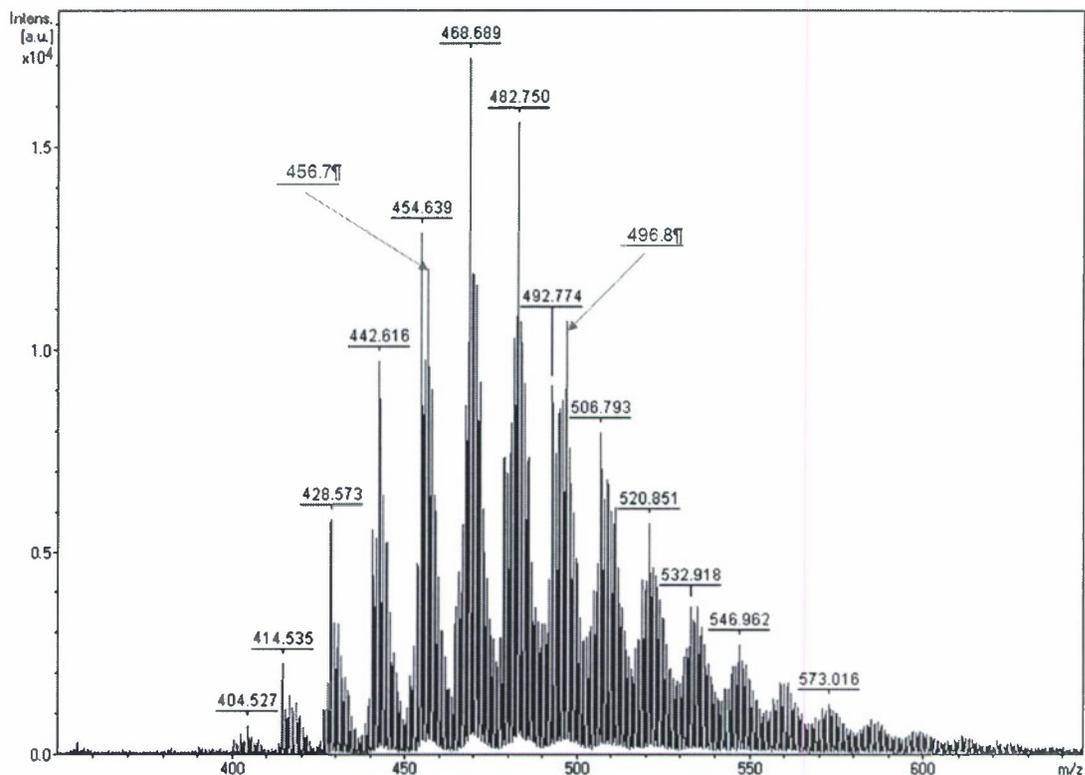


Fig. 14 – PSD results for the series of PAHs beginning with isomers of benzo[fluoranthene and with benzo[e]pyrene ( $m/z = 252.4$ ): (a) base aromatic structure; (b-d) one to three methyl substituents, respectively; (e) limited ethyl substituents may also be present.



**Fig. 15 – MALDI mass spectrum for the 97% dimer PF.**

monomeric species; thus, the benzofluorene may have been more prevalent in the original monomeric starting material. (4) Referring to the structures in Fig. 16, the most prevalent dimer species formed are not highly condensed, but in fact are relatively open structures. There would have to be a greater loss of H atoms than what is observed for a higher degree of condensation to occur.

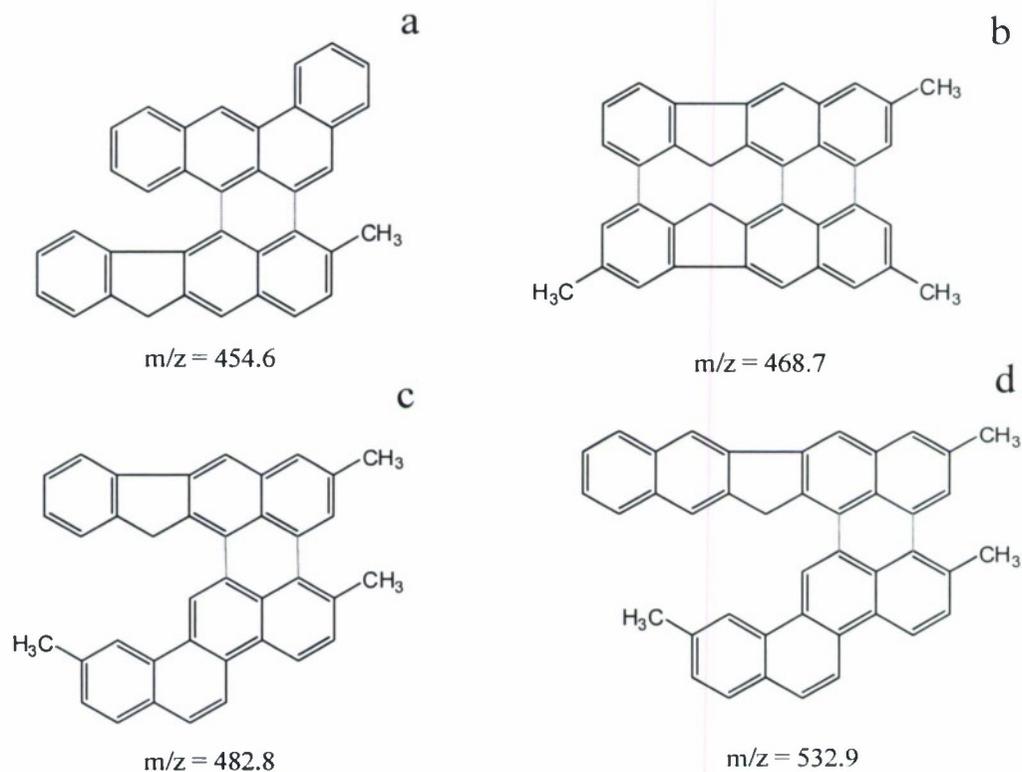
UV-Vis of the 97% dimer PF (Fig. 6) also supports the existence of relatively open PAH structures. A massive presence of extended aromatic structures in the dimer-rich vs. the monomer-rich PFs would drastically shift the absorption of visible light to higher wavelengths [24]. However, the “red shift”, although observable, is relatively small.

**Table 5 – Prominent peaks observed in MALDI mass spectrum for the 97% dimer PF (Fig. 15) can be explained by condensation of prominent peaks in MALDI of the 98% monomer PF (Fig. 10).**

| Monomer<br>Reactant 1<br>(m/z) | Monomer<br>Reactant 2<br>(m/z) | Hydrogen<br>Atom Loss | Dimer<br>Product<br>(m/z) |
|--------------------------------|--------------------------------|-----------------------|---------------------------|
| 216.4                          | 216.4                          | 4                     | 428.6                     |
| 216.4                          | 230.3                          | 4                     | 442.6                     |
| 216.4                          | 244.5                          | 6                     | 454.6                     |
| 228.3                          | 230.3                          | 4                     | 454.6                     |
| 216.4                          | 244.5                          | 4                     | 456.7                     |
| 230.3                          | 244.5                          | 6                     | 468.7                     |
| 228.3                          | 242.4                          | 2                     | 468.7                     |
| 244.5                          | 244.5                          | 6                     | 482.8                     |
| 230.3                          | 256.5                          | 4                     | 482.8                     |
| 216.4                          | 280.5                          | 4                     | 492.8                     |
| 244.5                          | 256.5                          | 4                     | 496.8                     |
| 256.5                          | 256.5                          | 6                     | 506.8                     |
| 244.5                          | 280.5                          | 4                     | 520.9                     |

#### 4. Conclusions

The characterization of petroleum pitches on a molecular level has long been a difficult task, but the separation of the pitch into its oligomeric fractions via dense-gas extraction (DGE), followed by the application of both new and conventional spectrometric and spectroscopic techniques to those fractions, has given us new capabilities for identifying the specific molecular structures in petroleum pitches. The monomer-rich fraction is approximately Gaussian with respect to mol wt and is dominated by species that are built upon a relatively small number of well-defined, PAH backbone structures. Methyl, and to a very limited extent ethyl groups decorate these backbones in an approximately Gaussian distribution, with dimethyl-substituted PAH molecules being the most common molecular makeup. The overall mol wt distribution of the dimer fraction is also approximately Gaussian, and the most prevalent species are consistent with combination of the most common monomer species via condensation, with the accompanying loss of 4-6 hydrogens. In previous work [11], we have shown that mesophase pitches which contain up to 25 mol % dimer can be produced by fractionation of M-50 pitch via DGE. Thus, to our knowledge this study represents the first time that researchers have proposed specific, “nonaverage” molecular structures that are significant constituents in mesophase pitch.



**Fig. 16 – Proposed PAH structures for the major constituents in the 97% dimer PF, see Table 5.**

### Acknowledgments

This work was supported by AFOSR (Contract No. FA9550-05-1-0060) and the Engineering Research Centers Program of the National Science Foundation under NSF Award Number EEC-9731680. The authors thank Eric Davis for his assistance with DGE experiments and with MALDI sample preparation; and Stephan Türk for his assistance with FD-MS analyses.

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