

QUANTITATIVE ANALYSIS OF CARBONACEOUS PITCHES USING MALDI MASS SPECTROMETRY

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Abstract

Matrix-Assisted, Laser Desorption/Ionization time-of-flight mass spectrometry (MALDI) is a promising technique for the absolute mol wt determination of carbonaceous pitches. Although MALDI spectra clearly indicate that separation of pitch into its oligomeric constituents is being obtained by Clemson's Dense Gas Extraction (DGE) process, the purity of the fractions isolated is still unknown because of a lack of calibration standards. Thus, we have initiated calibration studies by mixing dimer-rich and trimer-rich cuts obtained by DGE to synthesize mixtures of varying oligomeric compositions. In addition, a material balance on the DGE process itself, with MALDI being used for the analysis of the feed pitch and the top and bottom fractions, was also carried out. Results indicate that the response of MALDI is approximately proportional to mole fraction (vs. mass fraction), but pitch fractions significantly narrower than those produced to date will be necessary to more definitely establish this relationship.

Keywords: Petroleum pitch, Carbon precursor, Mesophase pitch, Analytical characterization

Introduction

Petroleum pitches can serve as precursors for advanced carbon materials, such as high thermal conductivity carbon fibers and carbon/carbon composites (Marsh et al., 1997). Research increasingly suggests that the molecular composition of the pitch has a significant impact on the properties and costs of the final carbon products. Dense Gas Extraction (DGE) is being developed at Clemson University (Edwards and Thies, 2006) for the fractionation of petroleum pitches, with the goal of controlling the oligomeric composition of the resultant fractions. Matrix-Assisted Laser Desorption/Ionization Time-of-flight Mass Spectrometry (MALDI) has been developed by our group for the absolute mol wt determination of carbonaceous pitches (Edwards and Thies, 2004), and the method has been used with good success in delineating, for the first time, the oligomeric nature of petroleum pitches. Furthermore, the use of MALDI has been critical for the development of DGE as a viable method for fractionating pitches, because before MALDI there was simply no reliable method for the accurate mol wt determination of the feed pitch, or the fractions obtained thereof.

One drawback of solid-based mass spectrometry (MS) techniques such as MALDI is the relative difficulty of obtaining quantitative results. In particular, a quantitative relationship between peak intensity and species mass is required if we are to determine the purity of the sample of interest. Based on both the theory of MALDI and the successful quantitative detection of biomolecules via this technique (Sarracino and Richert, 1996; Natori et al. 2006), we have been assuming that the area fraction under the MALDI spectra represents mole fraction. In this work, two pitch fractions isolated by DGE, one rich in dimer species and the other in trimers, were used to test this assumption. Also, a material balance study on an experimental DGE run was carried out, with MALDI being used to analyze the feed, top, and bottom fractions.

Experimental

Materials

Several pitch fractions obtained from the DGE of petroleum pitch, M-50 (CAS 68187-58-6), were used in this work. In particular, a dimer-rich and trimer-rich fraction were used for the calibration study, and a top and bottom cut obtained from a single DGE run were used for the material balance study. 7,7,8,8-tetracyanoquinodimethane (CAS 1518-16-7) was obtained from TCI America and used as a matrix for MALDI analysis. Deionized water was used for the MALDI sample preparation.

Sample Preparation and MALDI Analysis

For MALDI sample preparation, we took approximately 10 mg of pitch sample and added approximately 200 mg of the matrix TCNQ. For the calibration study, the dimer-rich and trimer-rich fractions were mixed in various proportions with the matrix in a single step. For example, 8 mg of dimer-rich fraction and 2.1 mg of trimer-rich fraction were mixed together to prepare Mixture 1, consisting of 84 area % dimer-rich fraction. We note the assumption of MALDI area fraction equaling mole fraction must be made to perform this calculation, as the number average mol wts for the dimer-rich ($\bar{M}_n = 640$) and trimer-rich fractions ($\bar{M}_n = 877$) are required to determine the moles of each oligomeric species present. Mixing was done using a grinding mill (Thermo Electron Corp., model Wig-L-Bug). Then the samples were spotted on the MALDI target plate using a water-spotting method (Edwards and Thies, 2005). For the material balance study, sample preparation for the MALDI analysis was done as described above.

All samples were analyzed using a Bruker Daltonics Autoflex MALDI-TOF mass spectrometer, which is equipped with 337 nm nitrogen laser. The reflector mode was used for this study. The target plate was positively charged and set to 19.0 kV; the secondary ion source to 17.5 kV, the lense to 7.65 kV, and the reflector to 20 kV. Ions generated after laser bombardment were accelerated using pulsed ion extraction after a time delay of 80 ns. Other important parameters used during the analysis were a detector gain of 5.0x, resolution of 2.0, and a mol wt suppression up to 250.

Optimal laser power was obtained by trial and error. We used laser powers ranging from 14 to 18% for the calibration study of dimer-rich and trimer-rich fractions and of their mixtures. For the material balance study, laser powers ranging from 20 to 22% were used. MALDI analysis done on different days with the same operating conditions can exhibit slightly different results because of the sensitivity of the instrument (Cervo and Thies, 2007). Hence all MALDI analyses for each of the two studies were done on same day.

Results and Discussion

MALDI Calibration Study with Dimer-rich and Trimer-rich Fractions and their Mixtures

MALDI spectra for the dimer- and trimer-rich fractions, and with mixtures thereof, are shown in Fig. 1. It is observed that MALDI spectra for all three mixtures lie in between the individual MALDI spectra for the dimer- and trimer-rich fractions.

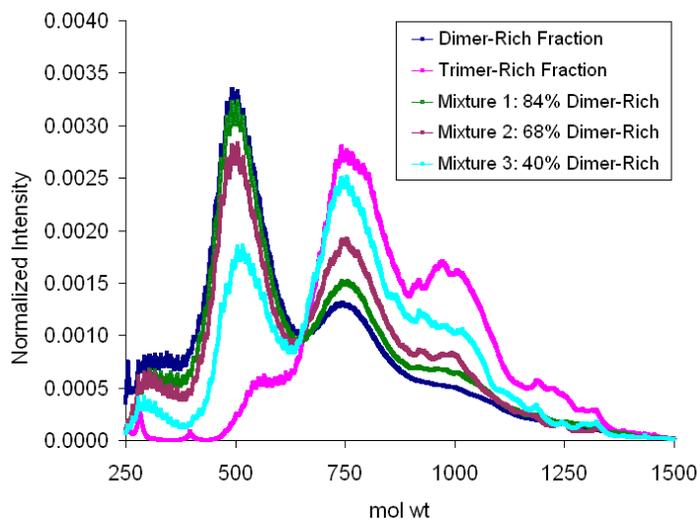


Figure 1. MALDI mass spectra for Mixtures 1, 2 and 3 of the dimer rich and trimer rich fractions.

To calculate oligomeric compositions, we assumed that the area under the MALDI spectra for each oligomer (see Table 1) represented mole fraction. Knowing the mole fractions of the oligomeric constituents of the dimer-rich and trimer-rich fractions, and knowing the amounts of these two fractions in each of the three mixtures; we can calculate the mole fraction of each oligomer in each mixture from a simple mole balance. Inherent in this calculation is a key assumption, namely that the species respond in the mixture in the same way that they responded in the fractions.

Table 1. Oligomeric Makeup and Mol Wt Ranges for Dimer-Rich and Trimer-Rich Fractions.

Pitch Oligomer	Mol Wt range	MALDI Area Fraction	
		Dimer-Rich fraction	Trimer-Rich fraction
Monomer	250-375	0.085	0
Dimer	375-625	0.49	0.065
Trimer	625-875	0.265	0.49
Tetramer	875-1125	0.12	0.34
Pentamer	1125-1375	0.04	0.095
> Pentamer	above 1375	0	0.01

We then independently determined the mole fraction for each oligomer in each of the three mixtures analytically, that is, by MALDI analysis of each mixture. Both analyzed and calculated values of mol fraction for Mixture 1 are shown in Table 2 below. Note that the analyzed values of oligomeric mole fractions, obtained from MALDI spectra, are generally within 20% of the calculated values. Similar results were obtained for all three mixtures.

A similar study to that described above was carried out with the assumption that MALDI spectra represent the mass fraction (instead of mole fraction) of the oligomeric constituents; in that case, the summation of errors squared was 3-4 times larger than for the mole fraction assumption.

Table 2. Oligomeric mole fractions in Mixture 1 as obtained by MALDI analysis are compared to mole fractions calculated from summing oligomeric compositions of dimer- and trimer-rich fractions (see Table 1).

Pitch Oligomer	Mixture 1 Analyzed Mol Frac	Mixture 1 Calc Mol Frac
Monomer	0.05	0.06
Dimer	0.39	0.35
Trimer	0.35	0.34
Tetramer	0.17	0.19
Pentamer	0.04	0.06
> Pentamer	0.00	0.00

Material balance study

The second study to assess the validity of the mole fraction equals area fraction for MALDI was a material balance study for an experimental DGE run, in which a feed pitch was fractionated into top and bottom cuts at extraction conditions of 350 °C, 750 psig, and a toluene-to-pitch ratio of 5:1 (see Fig. 2).

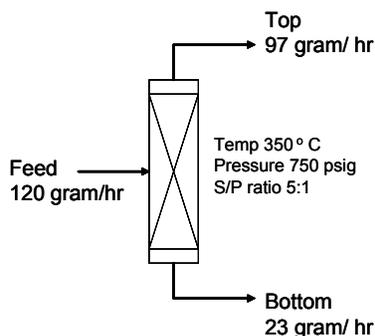


Figure 2. Schematic of DGE experiment.

The mass flow rates of all streams were accurately measured to within $\pm 2\%$. Feed, top, and bottom were analyzed by MALDI (Fig. 3). Using the MALDI spectra, \overline{M}_n were calculated for each stream (Table 3). Molar flow rates for each stream were then calculated. Using the area equals mole fraction assumption for MALDI, molar flow rates for each pitch oligomer were calculated for all three streams, feed, top, and bottom. With these results, a comparison can be made between the flow rates obtained from summing the top and bottom cuts vs the feed flow rate (see Table 4). Except for the monomer species, agreement between the two methods is to within 25%. In

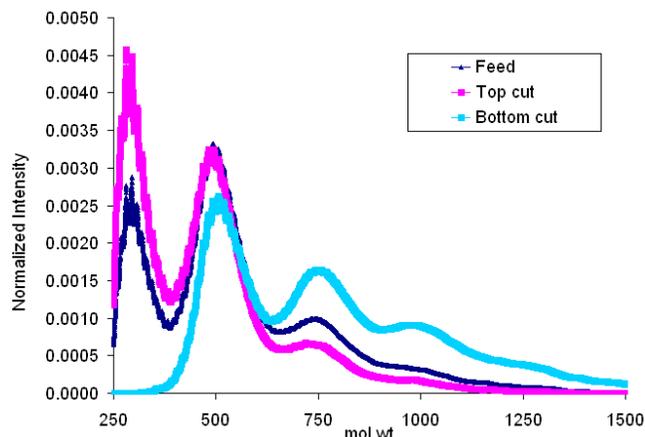


Figure 3. MALDI mass spectra for feed, top, and bottom cuts from DGE experiment.

Table 3. \overline{M}_n for each constituent oligomer and overall \overline{M}_n for Feed, Top and Bottom Cuts.

Oligomer	Feed \overline{M}_n	Top Cut \overline{M}_n	Bottom Cut \overline{M}_n
Monomer	307	305	353
Dimer	503	495	520
Trimer	744	738	753
Tetramer	985	981	995
Pentamer	1237	1223	1240
> Pentamer	1452	1503	1466
Overall	561	484	785

Table 4. Material balance study for DGE experiment shown in Fig 2. Oligomer molar flow rates are given per hour.

Pitch Oligomer	Moles in Top cut	Moles in Bottom cut	Moles in Top + Bottom	Moles in Feed
Monomer	0.070	0.000	0.070	0.047
Dimer	0.096	0.010	0.106	0.103
Trimer	0.026	0.009	0.035	0.043
Tetramer	0.007	0.006	0.013	0.016
Pentamer	0.001	0.003	0.004	0.005
> Pentamer	0.000	0.001	0.001	0.000
Total	0.201	0.029	0.230	0.214

summary, both of the above studies indicate that our current method of assuming MALDI area fraction equals mole fraction yields reasonable estimates of the molecular composition of petroleum pitches and their fractions.

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