

## TWO-DIMENSIONAL HPLC ANALYSIS OF FCC DECANT OILS

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### INTRODUCTION

Fluid catalytic cracking decant oils (FCC-DO) are used as feedstocks for producing highly graphitizable petroleum cokes (needle cokes) in delayed cokers<sup>1</sup>. The chemical composition of decant oils depends on the nature of catalytic cracker feeds and the conditions used in the crackers. It is known that the quality of the needle coke product is, in turn, strongly dependent on the chemical constitution of the starting decant oil. Therefore, the need for a detailed analysis of FCC-DO is well recognized; elemental analysis, various solvent fractionation techniques, NMR, and gas chromatography and gas chromatography/mass spectrometry (GC/MS) have been used to analyze these materials<sup>2,3</sup>. One limitation of ordinary GC and GC/MS methods is that heavy ends and some polar compounds cannot be analyzed because of their low volatility.

High performance liquid chromatography (HPLC) and HPLC/MS can be used to separate and analyze high molecular weight and polar fractions of feedstocks<sup>4,5</sup>. However, traditional HPLC instruments with mono-UV wavelength detectors are not amenable to identify the molecular components of the fractions eluted from the LC columns. The development of on-line HPLC/MS has greatly facilitated the analysis of heavy hydrocarbons without, however, the capability of distinguishing between the isomers of polycyclic aromatic compounds<sup>6</sup>. A distinct advantage of a two dimensional HPLC technique, which provides UV spectra of separated fractions as a function of time, is its capability to identify the molecular components of the eluates, including the isomers of polycyclic aromatic compounds. In this paper, we present the results of a two dimensional HPLC and heated probe/MS analyses of some FCC-DO samples.

### EXPERIMENTAL

HPLC analyses were carried out with a Waters 600 micro-flow syringe pump and a 4.6x150 mm column packed with C-18 stationary phase. A Waters Model 990 UV detector was used to collect UV spectra ranging from 200 nm to 400 nm. A mixture of distilled water and acetonitrile (EM Science, HPLC grade) was used as mobile phase. Decant oil samples and some model compounds were diluted in acetonitrile (4 µg/µL), and 1 µL sample was injected. The scan time used was 50 ms and every four scans were averaged to obtain a UV spectrum. At a column temperature of 50 °C and mobile phase flow rate of 1 mL/minute, the separation of components took 40-50 minutes, collecting 2400-3000 UV spectra during each analysis. Two dimensional and contour graphs as well as single UV spectra obtained from each analysis were plotted and studied.

Selected FCC-DO were also analyzed by a heated probe/MS technique to assist in component identification. A KRATOS MFC 1500 instrument was used for these analyses with electron impact ionization potential of 70 eV. Samples were placed in a probe which was introduced into the MS source. The probe was heated from 50°C to 250°C at a heating rate of approximately 15°C/min and mass spectra were collected at every 2.5 °C temperature interval during heating.

### RESULTS AND DISCUSSION

Before analyzing the FCC-DO samples, mixtures of six model compounds were analyzed by HPLC. Figure 1a and 1b show the two dimensional plots of the two ternary mixtures of naphthalene/anthracene/fluoranthene and phenanthrene/pyrene/chrysene, respectively. The

abscissa in the plots represents the retention time in the column, and the ordinate shows the UV wavelength. The UV absorption intensity is shown on the z axis. Samples of naphthalene, anthracene and fluoranthene were eluted at 4.90, 8.45 and 10.45 minutes, respectively, and well separated, as shown at the top of Figure 1. Similarly, phenanthrene, pyrene and chrysene, shown at the bottom of Figure 1, are also well separated with retention times of 7.75, 10.90 and 14.20 minutes, respectively. In addition to the different retention times, these six model compounds have distinctly different UV spectra which facilitate their positive identification in a mixture. For example, the isomers, phenanthrene and anthracene which give exactly the same mass spectra have quite different UV absorption characteristics; and pyrene and its homologues can be easily identified by the peaks located around the 340 nm region.

Figure 2 shows a classification of various PAH's according to the number of rings, cata- and peri-condensation, and linear versus angular configurations which are responsible for different UV absorption characteristics. For each aromatic compound shown in Figure 2, UV absorption wavelength increases as the number of aromatic rings increases. Also, one can distinguish between the aromatics of the same ring number with respect to differences in their molecular configurations, e.g., linear PAH's extend their absorption to the longer UV wavelengths than the angular PAH's.

A good separation of the components of the FCC-DO samples was obtained at a column temperature of 50°C and water/acetonitrile ratio of 2/3. Adding water to acetonitrile up to an optimum 40% in the mixture steadily improved the separation of the constituent compounds. All the FCC-DO samples were analyzed under the same conditions.

Figure 3 shows a two-dimensional plot of the HPLC results obtained for FCC-DO #1, indicating the series of identified compounds. One should note that the UV absorption intensities for the components in a mixture should not be taken as a quantitative measure of concentrations, since the observed intensity is not only a function of concentration, but also a function of molecular structure for each compound. Figure 4 shows the data for FCC-DO #1 as a contour graph. Contour lines in Figure 4 represent UV absorption intensities as a function of retention time and wavelength. The more lines cross a given region, the higher is the absorption intensity. One can see in Figure 4 that the highest intensity peaks are located at retention times of 11, 15 and 16 minutes. Peaks located around 21-22 minutes also appear as relatively strong but broad peaks. The use of a contour plot for plotting the data makes it easy to determine the right wavelength through which a representative HPLC chromatogram can be obtained. The trace shown at the bottom of Figure 4 is an HPLC chromatogram of the sample at a UV wavelength of 254 nm, showing a good separation of the constituent compounds. One should note that the identified compounds in Figure 4 are only the aromatic compounds present in FCC-DO #1, since aliphatic compounds do not absorb UV radiation in the wavelength range studied here. It is known that decant oils can contain high concentrations of paraffins and alicyclic compounds<sup>2,3</sup>.

The UV spectra corresponding to the retention times of strong peaks seen in Figure 4 are plotted in Figure 5 to identify the individual compounds with respect to their retention time and the attendant UV spectra. The solid line in Figure 5a is assigned to phenanthrene. The spectrum shown with a dotted line in Figure 5a is assigned to pyrene structures. As different from the spectrum of pure pyrene, the dotted line trace has a shoulder at 260 nm which may be assigned to alkyl substituted pyrenes or phenanthrenes. The third spectrum shown in Figure 5a with a broken line can be attributed to chrysene and benzo(c)phenanthrene. Any contribution from naphthacene or benzo(a)anthracene can be ruled out, since there is no UV absorption beyond 340 nm in this spectrum. All of these four ring aromatics have the same molecular weight of 228.29 and similar fragmentation patterns which make their differentiation by mass spectroscopy very difficult.

Figure 5b shows the UV spectra obtained at retention times of 15.15, 16.10 and 21.80 minutes. The three spectra obtained at retention times of 15.15 minutes (solid line), 16.1 minutes (dotted line), and 21.8 minutes (broken line) have similar traces to the pyrene spectrum with a clear shift to longer wavelengths, and can be assigned to benzo- and alkyl- pyrenes. One should note again

that MS alone would not readily distinguish between the alkyl substituted homologues of pyrene, fluoranthene, 1,2-benzofluorene, and 3,4-benzofluorene. The molecular weight of pyrene and fluoranthene is 202.26, benzofluorenes is 216.28 and the alkylated homologues of these compounds have molecular weights of 216.28, 230.29, 244.31 and 258.33, etc., with similar fragmentation patterns.

To compare with the HPLC data, a heated probe/mass spectroscopy analysis was carried out on the same decant oil sample. The collection of mass spectra was started at 50 °C, obtaining one mass spectrum at every 2.5 °C interval up to 250 °C. As the probe temperature increased, the decant oil sample evaporated gradually starting with lower boiling point fractions and progressing to higher boiling materials with reasonable separation. Major compounds in FCC-DO #1 were identified by their mass spectra, pointing out the two most dominant compound series. One series has  $m/z=202+14n$  ( $n=0,1,2,3...$ ) (pyrene+ alkylpyrenes), and the other has  $m/z=252+14n$  ( $n=0,1,2,3...$ ) (benzopyrene + alkylbenzopyrenes). Typical mass spectra of these compound series collected at probe temperatures of 70 °C and 120 °C are shown in Figure 6a and 6b, respectively. Although the separation processes involved in HPLC and heated probe/MS are different, the general order of compounds released from LC column and the heated probe appears to be the same, controlled apparently by the molecular weight of the constituent molecules.

Comparing the HPLC and heated probe/MS data, one can see that the first major HPLC fraction eluting at 11 minutes is pyrene (MW=202.26), which corresponds to a probe temperature of 70 °C in the mass source. As the temperature of the probe increases, compounds with  $m/z=228+14n$  ( $n=0,1,2,3...$ ) emerge starting with chrysene (MW=228.29) detected at HPLC elution time of 14.2 minutes, followed by the second major fraction with  $m/z=252+14n$  ( $n=0,1,2,3...$ ) namely, benzopyrene at 15.2 minutes and alkylbenzopyrenes starting at 16.1 minutes of LC retention time. At a probe temperature of 165 °C, a compound series of  $m/z=290+14n$  ( $n=0,1,2,3...$ ) appears with a corresponding LC retention time of 21.8 minute, assigned as dibenzopyrene and its alkyl homologues.

Figure 7 shows the contour plots of the HPLC data on two other decant oil samples, FCC-DO #2 and FCC-DO #3. By comparing the contour graphs of the three decant oil samples, one can clearly see that FCC-DO #2 and FCC-DO #3 contain more lower molecular weight aromatic compounds than FCC-DO #1. These lighter compounds consist of naphthalene, alkylnaphthalenes, phenanthrene and alkylphenanthrenes, which were eluted from the HPLC column in less than 10 minutes.

## CONCLUSIONS

A two-dimensional HPLC technique is useful for separation and identification of aromatic compounds present in fluid catalytic cracking decant oils. This method combined with a heated probe/MS analysis provides a positive, and convenient identification of high-molecular-weight aromatic compounds. The analysis of three different FCC-DO's has shown significant variations in the composition of their aromatic fractions.

## ACKNOWLEDGEMENTS

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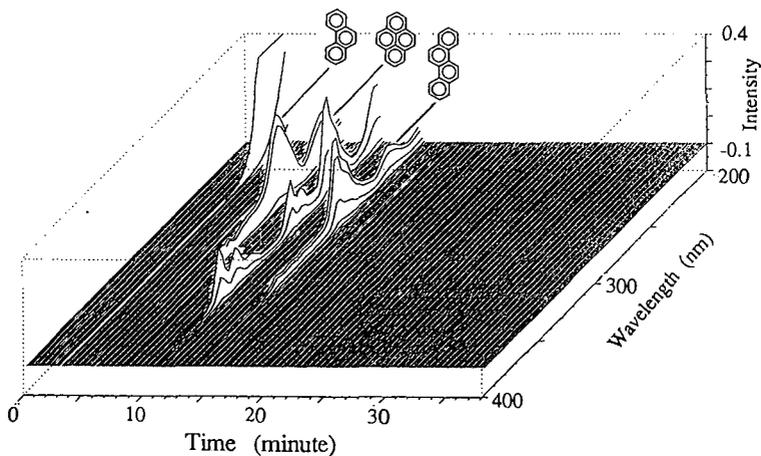
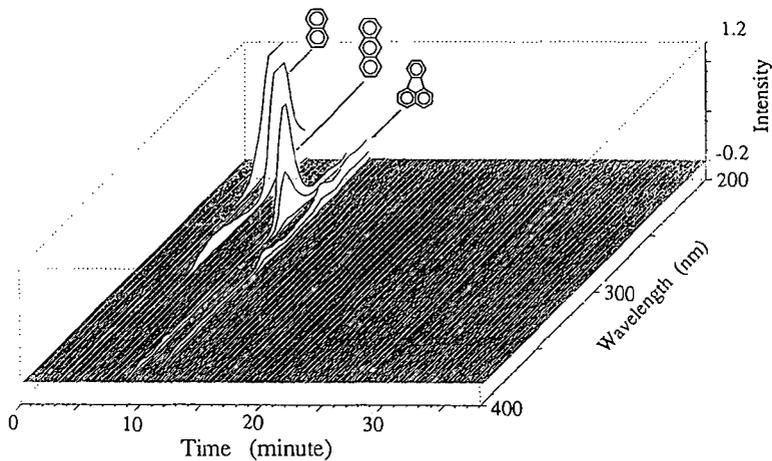


Figure 1. Two-dimensional HPLC plots for the two ternary mixtures naphthalene/anthracene/fluoranthene (top, a) and phenanthrene/pyrene/chrysene (bottom, b).

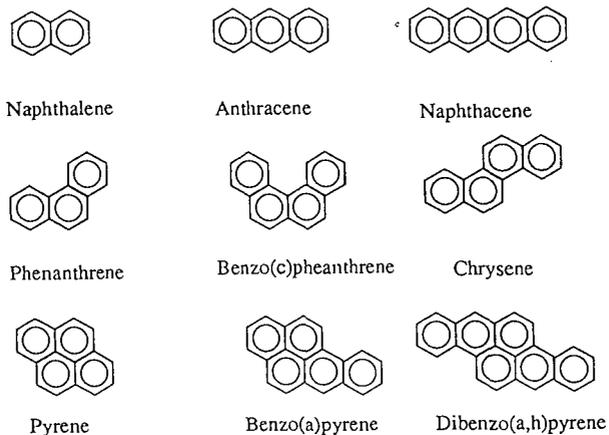


Figure 2. Different aromatic compounds found in FCC-DO.

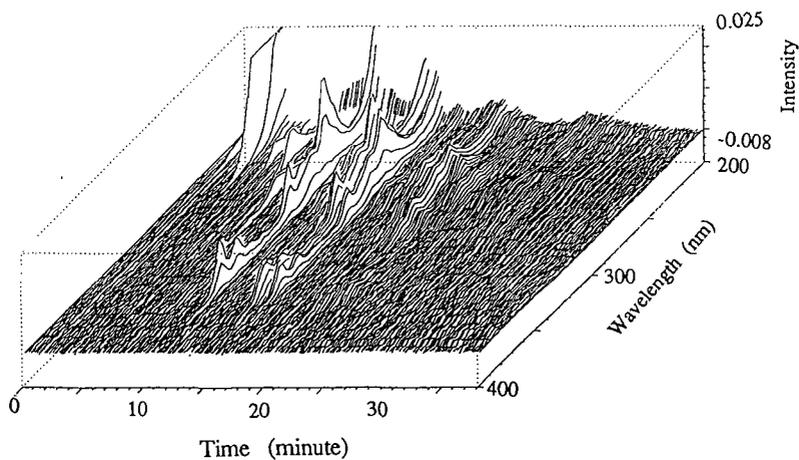


Figure 3. Two-dimensional HPLC plots for the sample FCC-DO #1.

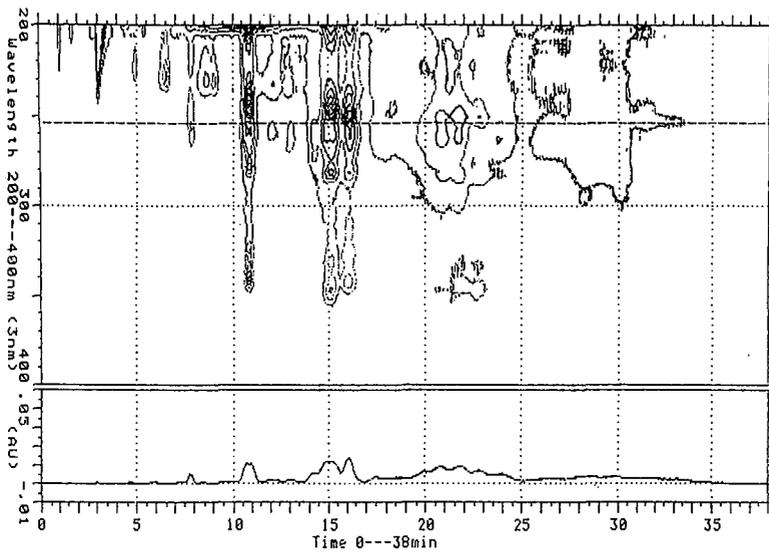


Figure 4. The HPLC contour plot for FCC-DO #1.

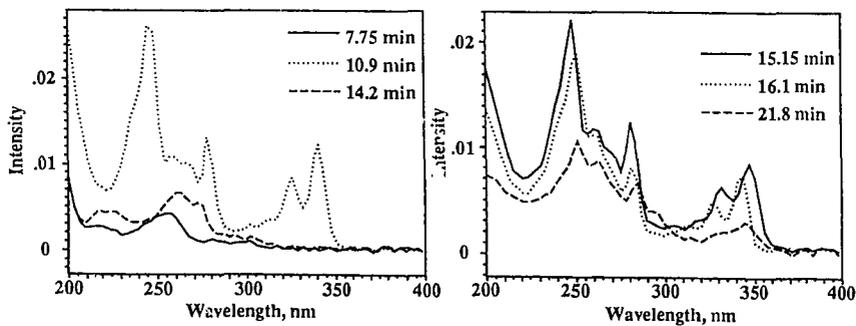


Figure 5. UV spectra of the compounds which elute at the indicated retention times.

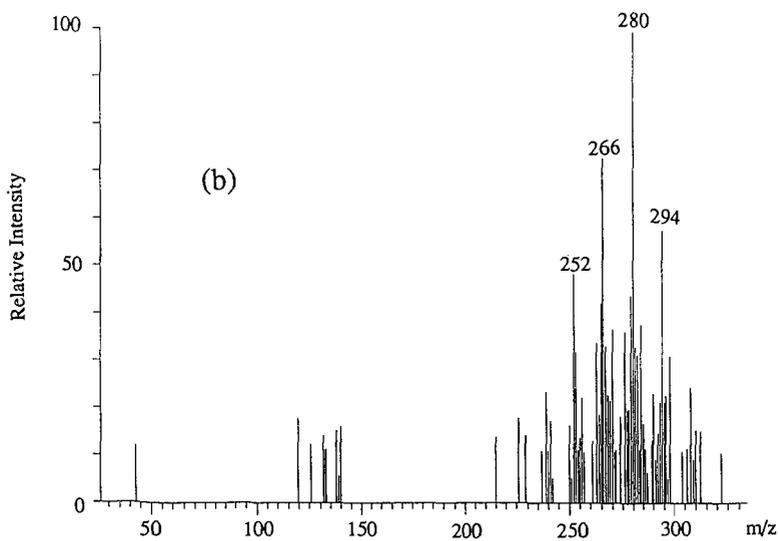
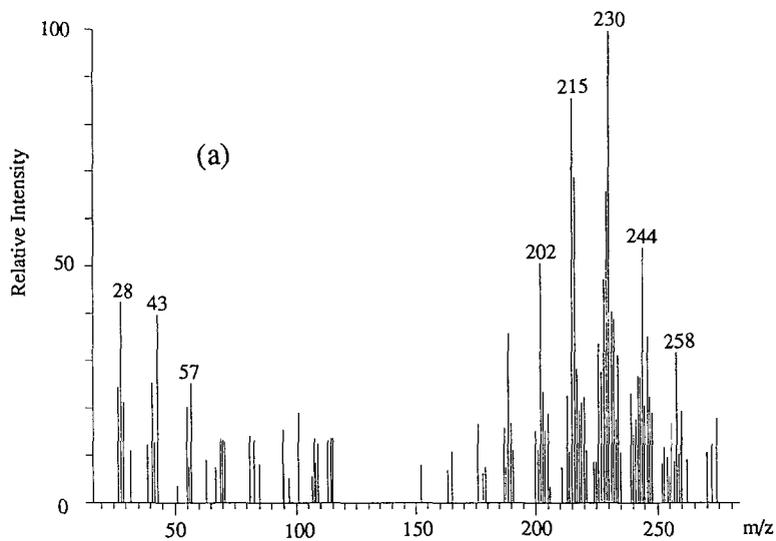


Figure 6. Mass spectra for sample FCC-DO #1 from the heated probe/MS experiment.

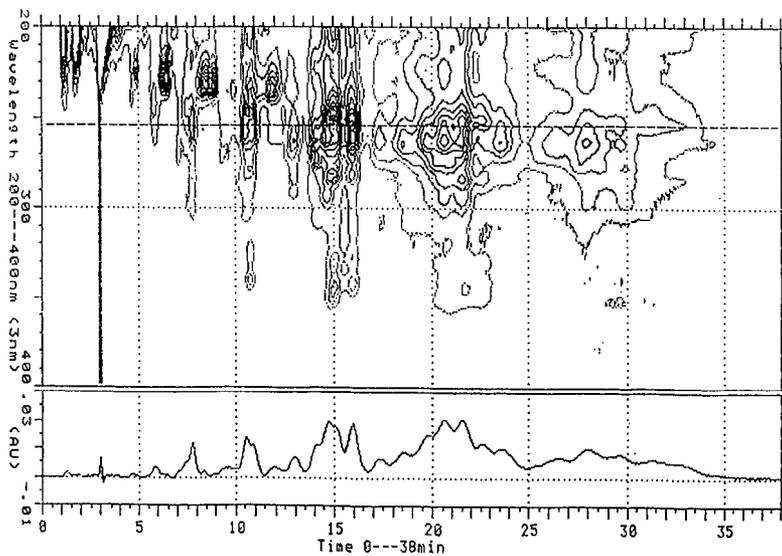
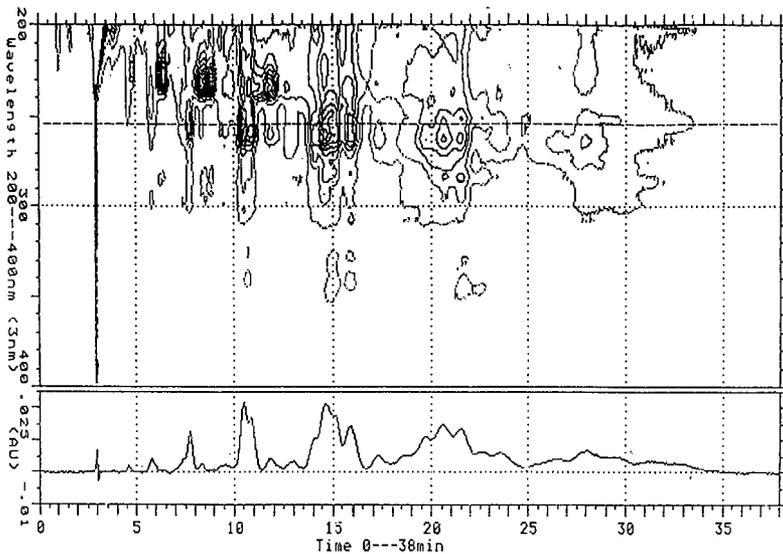


Figure 7. The HPLC contour plot for FCC-DO #2 (top) and FCC-DO #3 (bottom).