

A GC/MS ANALYSIS AND CARBONIZATION OF DECANT OILS

S. Eser and Y. Liu

Fuel Science Program, The Pennsylvania State University
209 Academic Projects Building, University Park, PA 16802

ABSTRACT

Six fluid catalytic cracker decant oils (FCC-DO) samples were characterized by gas chromatography/mass spectroscopy (GC/MS) and carbonized to study the relationships between the chemical constitution and the optical texture of derived needle cokes. Ion chromatograms for each sample were studied, and more than 50 molecular and fragment ions were selected for a semi-quantitative analysis. Although the GC/MS technique and the selected ion integration method used have certain limitations, some correlation was observed between the chemical constitution of the decant oils and the quality of the resulting needle cokes.

INTRODUCTION

Fluid catalytic cracker decant oil is used as feedstock to produce premium needle cokes. However, FCC decant oils may have significantly different chemical composition and carbonization behavior(1). Gas chromatography(GC) and size exclusion chromatography(SEC) were used to characterize carbonization feedstocks(2, 3). Recently, two-dimensional high performance liquid chromatography(HPLC) and heated probe MS analysis were developed and applied to FCC decant oil characterization(4). The reported results indicate that compounds up to seven or eight ring aromatics are found in decant oils, but in general, three and four ring aromatics and long chain normal alkanes were found to be the dominant components in decant oils(4). These results suggest that the distribution of major components in decant oil can be studied by GC/MS methods. In this study, six samples from four decant oil sources were analyzed by GC/MS using the selected ion integration method. The Carbonizations of decant oils were also carried out to study the relationships between chemical constitution of decant oils and resulting semi-cokes.

EXPERIMENTAL

GC/MS analysis was carried out on FCC decant oil samples designated FDO #1 to FDO #6. FDO #1 and FDO #2 were received from the same source but at different time, as were samples FDO #5 and #6. An HP 5890 Gas

Chromatography interfaced to an HP 5971A Mass Selective Detector was employed. The samples were dissolved in chloroform and injected, using the splitless mode, into a J&W DB-17 GC column. The GC column temperature was controlled from 40 °C to 280 °C at heating rate of 4 °C/min.

Decant oils were carbonized in tubing reactors at 500 °C for 3 hours under a nitrogen atmosphere. Semi-cokes obtained after carbonization were embedded in epoxy resin and polished using conventional techniques. A polarized-light microscope (nikon-microphot-FXA II) was used to examine the optical textures of resultant semi-cokes.

RESULTS AND DISCUSSION

A GC/MS total ion chromatogram (TIC) for samples FDO #1 to FDO #6 are shown in Figure 1. Most abundant ion peaks in FDO #1 and #2 are normal alkanes. Aromatic compounds become gradually important in going from FDO #1 to FDO #6. The dominant compounds in samples FDO #5 and #6 are pyrene and its methyl substituted analogs. For all the samples, constituent compounds consist of two to four ring aromatics with different degrees of ring substitution. The GC/MS TIC shows a hump of unresolved peaks around 45 to 65 minutes of retention time for each sample. A method of using selected ion chromatograms was employed to resolve the overlapping peaks.

Selected Ion Chromatograms(SIC) of mass 57, a stable aliphatic fragment, for samples FDO #1 to FDO # 6 are shown in Figure 2. All the samples show a long chain alkane distribution from C16 to C32 except sample FDO #4, which shows a significant shift towards the lower molecular weight alkanes (C12-C26). Sample FDO #3 shows a bimodal distribution of normal alkanes.

All the major aromatic peaks have been identified by mass spectroscopy. They are categorized into four series of compounds: naphthalenes, three ring aromatics (phenanthrene and anthracene), peri- and cata- four condensed ring aromatic compounds. Chromatograms of selected ions for these compounds, including alkyl substituted analogs and alkanes for FDO #3, are plotted in Figure 3. The labels "A, B, C, D" following ion mass numbers represent different isomers of the same compound. Table 1 gives the compound identification of the mass numbers used in Figure 3. Integrated intensities for ions of mass 55, 57, 69, 71, 83, 85, 97, 99 and 113 were obtained from one peak, the maximum alkane peak in each MS chromatogram.

The areas for isomers from each ion were added and the sum was divided by the area of the pyrene peak for normalization. The distribution of these summed ratios is presented in Figure 4. Columns marked alkane

present the sum of peak area ratios for 55, 57, 69, 71, 83, 85, 97, 99 and 113. Samples FDO #1 and FDO #2 show similar component distributions. The alkane contents in these two samples are higher than the other samples. Furthermore, the three ring aromatics are the most abundant components in samples FDO #1 and #2. Samples FDO #1 and #2 produced inferior optical textures upon carbonization. In contrast, samples FDO #5 and #6 produced premium needle cokes. These two samples contain less alkanes than the other samples. The dominant components in FDO #5 and #6 are pyrene and alkyl pyrenes. Sample FDO #3 contains more alkanes than FDO #4, but the former sample produced significantly better semi-coke than the latter. This implies that alkane composition may not be the only factor to affect needle coke quality. Both aliphatic and aromatic component distributions for sample FDO #4 are shifted toward lower molecular weight compound direction. This reveals why FDO #4 produced poor semi-coke.

REFERENCE

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Table 1. List of selected ions

Mass	compound's name
128	Naphthalene
142	Naphthalene -methyl
156	Naphthalene -ethyl or dimethyl
170	Naphthalene -C3
178	Phenanthrene
192	Phenanthrene methyl
206	Phenanthrene ethyl or dimethyl
220	Phenanthrene - C3
202	Pyrene
216	Pyrene -methyl
230	Pyrene -ethyl or dimethyl
244	Pyrene -C3
228	chrysene
242	chrysene -methyl
256	chrysene -ethyl or dimethyl
270	chrysene -C3
55	n-C4 alkene
57	n-C4 alkane
69	n-C5 alkene
71	n-C5 alkane
83	n-C6 alkene
85	n-C6 alkane
97	n-C7 alkene
99	n-C7 alkane
113	n-C8 alkane

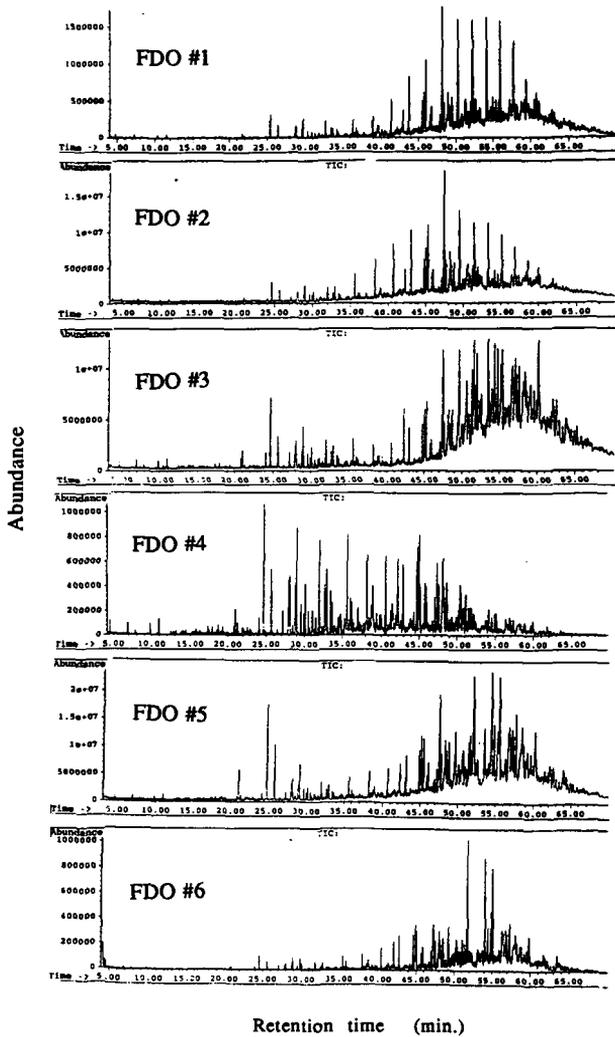


Figure 1. Total ion chromatograms for samples FDO #1 - #6

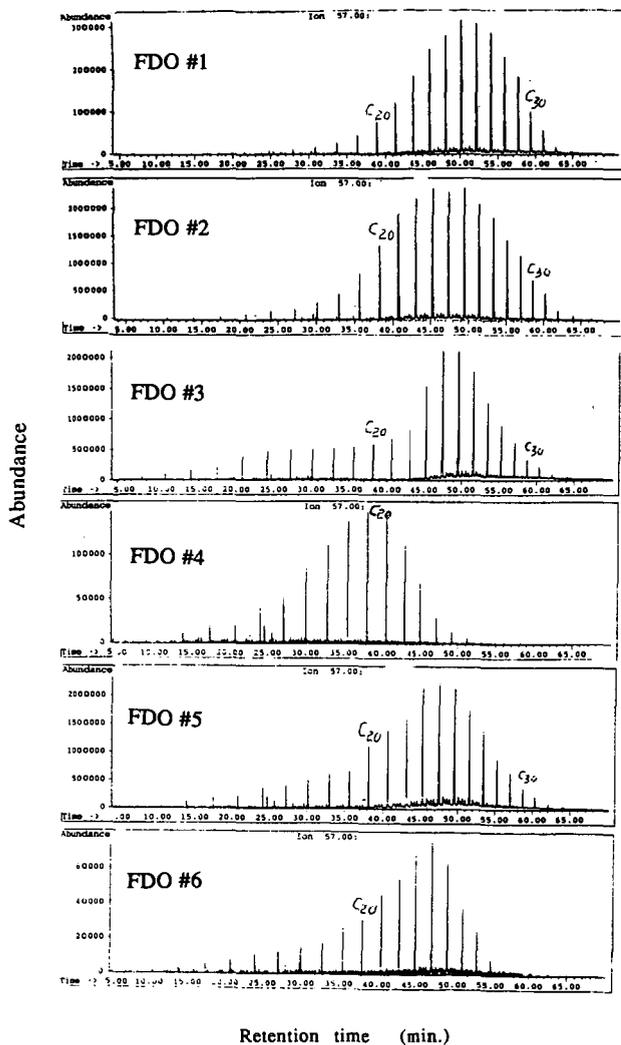
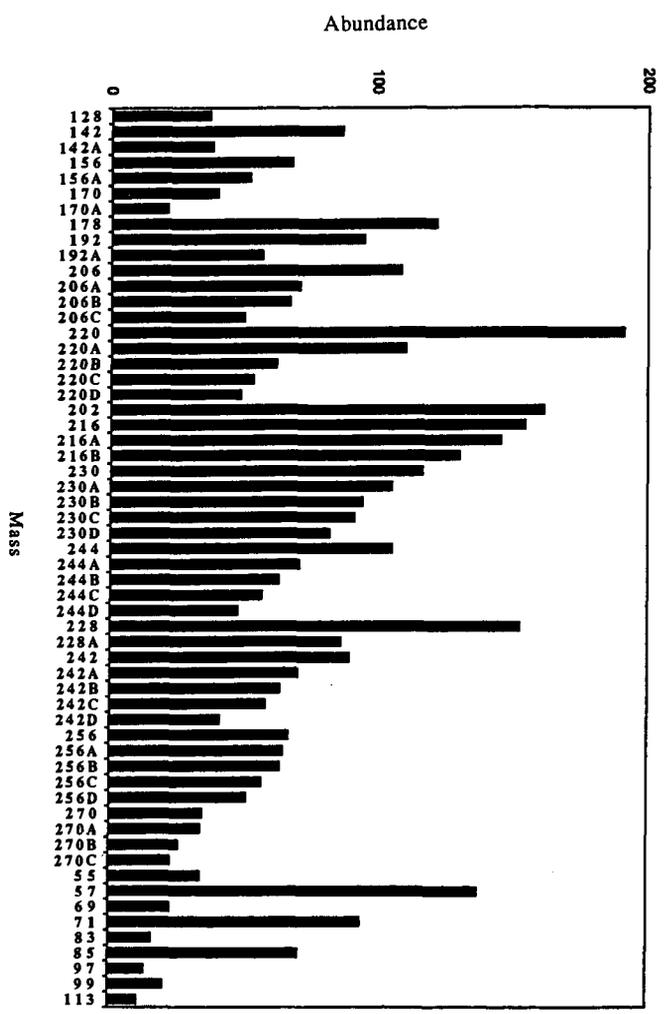


Figure 2. Selected ion (mass 57) chromatograms for FDO #1 - #6

Figure 3. A distribution of selected ions for decant oil FDO #3



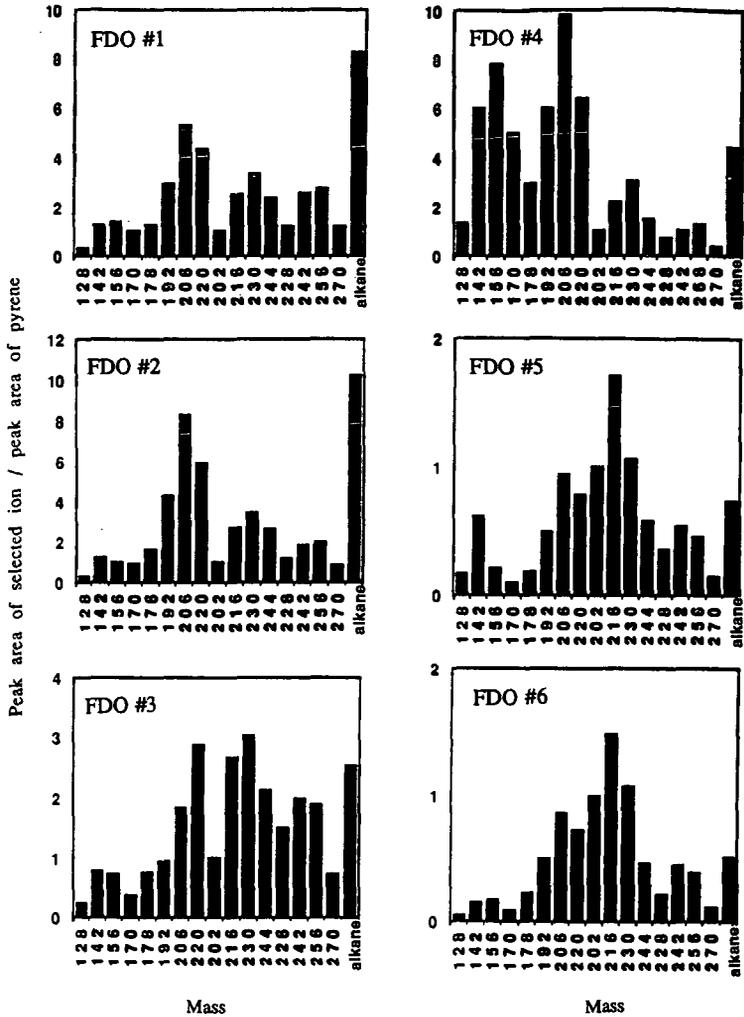


Figure 4. A distribution of selected ions for decant oil FDO #1 -#6