

REACTIONS OF HYDROCARBONS AND SULFUR COMPOUNDS DURING EARLY STAGES OF CARBONIZATION

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Introduction

Decant oils from fluid catalytic cracking are used as delayed coker feedstocks for production of needle cokes. Understanding the relationship between the chemical constitution and carbonization behavior of decant oils and the optical texture of the resulting coke is important for needle coke producers [1-3]. Several researchers have reported correlations between bulk properties, or averaged molecular parameters of feedstocks, such as solvent fractions and aromaticity, with the extent of mesophase development and resulting optical texture of the product cokes [4,5].

In the present work, three different decant oil samples, DO A, DO B, and DO C, and their early carbonization products were analyzed by quantitative GC/MS and by GC with dual detectors FID/FPD for enhanced detection of sulfur compounds. The main focus of the study is to understand how the molecular composition of decant oils influences both the microstructure of the semicokes formed, and the incorporation of sulfur into the semicokes.

Experimental

The three decant oils chosen for the study produced semicokes with different optical textures. DO A produces high quality needle coke, DO B gives a poor coke texture, and DO C gives a coke with intermediate optical texture. The decant oils were solvent fractionated by alumina column chromatography using sequential elution with hexane, benzene, and tetrahydrofuran / methanol (9:1), to obtain the bulk distribution of aliphatic, aromatic, and polar species. This data, along with other properties of the decant oils is given in Table 1.

Carbonization experiments were performed on approximately 5 grams of decant oil in 15 ml, closed tubing bomb reactors at 500°C in a preheated fluidized-sand bath for periods of 30-60 minutes. The decant oils and product maltenes (hexane solubles) were quantitatively analyzed by GC/MS using a procedure modified after EPA Method 8270b. The details of the analytical protocol have been reported [6]. Analyses were performed on an HP 5890 gas chromatograph (DB-5 fused silica column) interfaced to an HP 5971A mass selective detector using

electron ionization (70eV). The standard used for instrument calibration and for quantitation consisted of a 30 component mixture (Supelco, Inc., Bellefonte, PA; purchased as a custom standard) representative of PAH compounds and *n*-alkanes that are typically found in decant oils. Identifications of sulfur compounds were done by co-injection with a series of sulfur standards, including six dimethyldibenzothiophene (DMDBT) isomers (4,6-, 1,3-, 2,4-, 1,2-, 1,4-, and 2,3-DMDBT). A GC with a sulfur selective detector, a single flame FPD was used to identify the distribution of GC-amenable sulfur species in the decant oils.

Results and Discussion

The quantitative analysis of the decant oils resulted in characterization of 14wt%, 17wt% and 20wt% of DO A, DO B, and DO C, respectively. These amounts represent varying distributions of *n*-alkanes, 2-5 ring PAHs and the analogous alkylated PAHs, as shown in Figure 1. The *n*-alkanes were found in high concentrations in DO B, representing approximately 7wt% of the total feedstock. The *n*-alkanes are minor constituents of DO A (1wt%) and DO C (<1wt%), and were not detected in any sample after 30 minutes of reaction time.

DO A is characterized by high concentrations of pyrene, alkylpyrenes, and a moderate amount of alkyl substitution (methyl and dimethyl) of the main PAHs in this sample. This decant oil also contains the highest aliphatic content of the three samples used in this study. In contrast, DO B contains high concentrations of highly substituted PAHs. The most abundant alkylPAHs in DO B are tri- and tetra-substituted PAHs. The trialkylphenanthrenes are dominant components. Sample DO C is highly aromatic and contains high concentrations of unsubstituted PAHs, notably, phenanthrene, anthracene, fluoranthene, and pyrene. The dominant alkyl chain length on the major PAHs varied from methyl to trialkyl, and did not appear to follow any particular trend.

The relative distribution of PAHs changes dramatically during carbonization. Figure 1 shows the distribution of the main PAHs in the unreacted decant oils compared with the carbonization products from each sample. In all cases, several common trends are observed:

phenanthrene and methylphenanthrenes are present in high concentrations, the main alkyl group on PAHs is methyl, except for the naphthalenes, and the *n*-alkanes have been converted by 30 minutes reaction time. Only in the products from carbonization of DO A, however, are pyrene and methylpyrenes the major constituents. The products from DO B and DO C are dominated by phenanthrene, methylphenanthrenes, and low molecular weight naphthalenes. The carbonizing matrix of these two samples has relatively low concentrations of pyrene and alkylpyrenes.

The analysis of sulfur compounds centered around the alkyldibenzothiophenes (alkylDBTs) and alkylbenzothiothiophenes. The distribution of alkylated sulfur compounds followed the same pattern as the PAHs for each oil, e.g., DO B contains high concentrations of trialkyldibenzothiophenes. During early carbonization of DO A, there is a net production of DBT and methyl- and dimethylDBTs. By 60 minutes of carbonization, two methylDBT isomers (4-MDBT and 2-MDBT) are the main sulfur compounds in DO A. In contrast, the only sulfur compound present in significant amounts in the product maltenes from DO B and DO C, at all time periods, is NBT. The same sulfur compounds in DO B and DO C appear to be more readily consumed during early carbonization.

Conclusions

The decant oils used in this study have different molecular compositions that appear to have direct bearing on the quality of coke each produces. A moderate aromaticity, an abundance of pyrene and methylpyrenes, and lower degree of alkyl substitution in the DO A, coupled with high concentration of pyrene and methyl pyrenes (good solvents and H-shuttlers) in the carbonizing matrix, led to the well-developed texture. The inferior texture of DO B is attributed to the higher reactivity of its chemical constituents, i.e., *n*-alkanes, polyalkylated aromatics. The highly aromatic nature of DO C, combined with high concentrations of low molecular weight compounds in the carbonization products results in a coke with intermediate texture.

Acknowledgments

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References

1. Stocks, C.A. and Guercio, V.J., *Erdol Kohle Erdgas Petrochem.*, 1985, 31.
2. Mochida, I., Korai, Y., Fei, Y.Q., Oyama, T., *Oil and Gas Journal*, 1988, 73-77.

3. Nesumi, Y., Todo, Y., Oyama, T., Mochida, I., and Korai, Y., *Carbon*, 1989, 27, 359.
4. Rudnick, L.R. and Galya, L.G., *Energy Fuels*, 1991, 5, 733.
5. Eser, S. and Jenkins, R.G., *Carbon*, 1989, 27, 877.
6. Filley, R.M. and Eser, S., *Energy Fuels*, 1997, in press.

Table 1. Decant Oil Properties.

	DOA	DO B	DO C
sulfur content	0.70	0.23	0.42
asphaltenes	1.30	1.30	1.6
specific gravity	1.052	1.003	
quinoline insol.	0.01	0.00	0.02
aliphatic (%)	21	10	12
aromatic (%)	75	88	86
polar (%)	4	2	2

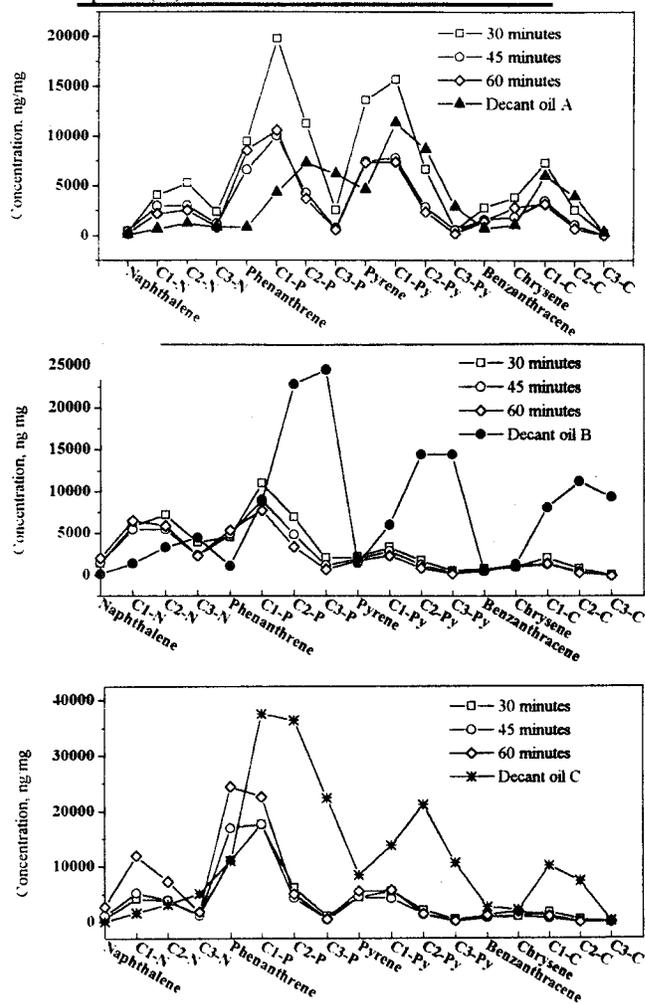


Figure 1. Distribution of major PAHs in unreacted decant oils compared with the respective product maltenes for (a) DO A (b) DO B and (c) DO C.