

Relationships between Molecular Composition of FCC Decant Oils and Mesophase Development

Yanlai Liu and Semih Eser

Fuel Science Program, 209 Academic Projects Building, Department of Materials Science and Engineering
The Pennsylvania State University, University Park, PA 16802, USA

Introduction

Petroleum feedstocks including pitches, vacuum distillation residua and FCC decant oils were characterized by various spectroscopic and chromatographic techniques [1-4]. Recently, it has become clear that the quality of petroleum cokes produced by delayed coking depends strongly on the molecular composition of the coker feedstocks [5,6]. We have used GC/MS, two-dimensional high performance liquid chromatography (HPLC), and heated probe/MS analysis in our laboratory to identify the molecular constituents of FCC decant oils [5-8]. Since three- and four-ring aromatics and normal alkanes constitute the bulk of most decant oils, GC/MS appears to be a useful tool to study the distribution of major components in decant oils. In this study, we report a statistical analysis of GC/MS data on eighteen FCC decant oil samples and the corresponding semi-coke texture to seek correlations between molecular constitution of the feedstocks and mesophase development during carbonization.

Experimental

Eighteen different decant oil samples were analyzed using an HP 5890 gas chromatograph interfaced to an HP 5971A mass selective detector. A J&W DB-17 GC column was used in all the analyses where the column temperature was controlled from 40 °C to 280 °C at a heating rate of 4 °C/min. The relative distribution of seven components (n-alkanes, naphthalenes, phenanthrenes, pyrenes, chrysenes, biphenyls, and fluorenes), including the alkylated homologs of the aromatic compounds, was calculated by comparing the integrated intensities of selected specific ion chromatograms (mass 71 was used to calculate the relative abundance of n-alkanes).

Decant oils were carbonized in closed tubing reactors at 500 °C for 3 hours under a nitrogen atmosphere. A polarized-light microscope (Nikon-Microphot-FXA II) was used to examine the optical textures of semi-cokes. An automated point counting procedure was used to characterize the optical texture of the semi-cokes using an optical texture index similar to that suggested by Marsh et al. [9].

Results and Discussion

Figure 1 shows a plot of the distribution of the seven groups of compounds (including the alkylated homologs of the aromatic compounds) for each

sample, indicating some grouping of the samples with respect to their chemical constitution.

The statistical correlations between seven GC-amenable components in feedstocks (n-alkanes, naphthalenes, phenanthrenes, pyrenes, chrysenes, biphenyls, and fluorenes) and the optical textures of derived semi-cokes are listed in Table 1. The optical texture index (OTI) was determined by point counting the mesophase structures in the semi-cokes. The larger the index value, the higher the anisotropy of the semi-coke. The four components in Table 1, naphthalenes, phenanthrenes, pyrenes and chrysenes show positive correlations to the optical texture index. Compared to naphthalene (0.3) and phenanthrene (0.2), pyrene (0.5) and chrysene (0.5) have higher correlation coefficient values, indicating both pyrene and chrysene have a higher rank influence on the mesophase development. Three components (n-alkanes, biphenyls and fluorenes) show negative correlations to the optical texture index. Among them, biphenyl (-0.7) has the highest negative correlation with OTI. Most likely, the free rotation between the two rings in biphenyl is responsible for the formation of a less developed optical texture in the cokes [10].

A multi-variable regression analysis was conducted to correlate the chemical composition of feedstocks and the optical textures of the derived semi-cokes. On the basis of the GC/MS results, the seven major components were selected as independent variables and a multiple linear regression equation with an R^2 value of 0.9 was obtained as follows:

$$\text{OTI} = (-0.2)\text{alk} + (1.33)\text{naph} + (0.1)\text{phen} + (0.98)\text{pyrene} + (0.64)\text{chrysene} + (-0.2)\text{biphenyl} + (3.44)\text{fluorene}$$

This equation represents only a good fit of the experimental data with linear regression, using a limited number of samples in a given set of FCC decant oils. Large positive coefficients for naphthalenes, pyrenes and chrysenes as well as negative coefficients for alkanes and biphenyl are in agreement with the statistical correlations given in Table 1. Considering the strong hydrogen shuttling and solvent properties of pyrenes and intermediate carbonization reactivities of naphthalenes and chrysenes, it is reasonable to expect positive correlations between the abundances of these compounds and the optical texture index. A

previous study also showed a very strong positive influence of pyrenes on the development of needle coke texture [7]. The negative effects of n-alkanes and biphenyls on mesophase development are also understandable based on the tendency of these compounds to form non-planar structures during carbonization. It is not clear, however, why fluorenes should have the largest positive coefficient for mesophase development, contrary to the negative correlation given in Table 1 and poor texture development obtained from the carbonization of fluorene itself. It is possible that fluorene may behave differently in a complex mixture of aromatic and aliphatic hydrocarbons to promote mesophase development or that the abundance of fluorenes may be related to the presence of some good actors in the non-GC amenable portion of the FCC decant oil samples. These are all speculations which need to be verified.

It can be argued that GC/MS analysis leaves out the heavy fractions of the decant oils which are probably the most important constituents for mesophase development. Considering, however, that most petroleum fractions represent a continuum in their chemical constitution, the molecular composition of the GC amenable fraction of the decant oils should be somehow related to that of the non-GC amenable fraction. This relationship can be established by molecular characterization of the heavy fractions by other chromatographic and spectroscopic techniques. More importantly, the significance of any correlation between the chemical constitution of the feedstocks and the optical texture of the resulting cokes has to be rationalized in terms of the complex chemistry of mesophase development.

References

1. H. Honda, Carbon **26**, 137, 1988.
2. S. Eser and R. G. Jenkins, Carbon **27**, 889, 1989.
3. I. Mochida, K. Shimizu and Y. Korai, Carbon **28**, 311 1990.
4. R. A. Greinke and L. S. Singer, Carbon **26**, 665, 1988.
5. Y. Liu, S. Eser, and P. G. Hatcher, Am. Chem. Soc., Div. Fuel Chem., Preprints **37**, 1227, 1992.
6. S. Eser and Y. Liu, Am. Chem. Soc., Div. Fuel Chem., Preprints **38**, 452, 1993.
7. Y. Liu and S. Eser, Extended Abstracts, 21st Biennial Conference on Carbon, 288, 1993.
8. T. Filley, P. Greenwood, and S. Eser, Extended Abstracts, 21st Biennial Conference on Carbon, 318, 1993.
9. H. Marsh, Editor, "Introduction to Carbon Science," p.20, Butterworths, 1989.
10. P. L. Walker, Jr., Chem. Ind. (London) **61**, 683, 1982.

Acknowledgements

Financial support for this study was provided by Unocal Corporation through Carbon Research Center at the Pennsylvania State University. Rose Filley and Timothy Filley helped with GC/MS analysis and carbonization experiments; Ronald M. Copenhaver helped with the preparation of the polished semi-coke pellets. The authors gratefully acknowledge a communication from Dennis M. Riggs of R J Reynolds Tobacco Company on the statistical analysis of the experimental data.

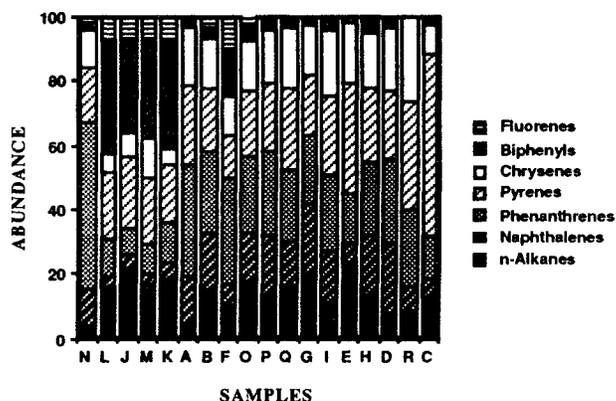


Figure 1. A distribution of the n-alkanes and selected aromatic compounds with their alkylated homologs in the feedstocks obtained from the integrated GC/MS data using selected specific ions.

Table 1. Correlation coefficients for the components of feedstocks and the optical texture index of resulting semi-cokes.

	Alk	Nap	Phe	Pyr	Chr	Bip	Flu	OTI
Alk	1.0							
Nap.	-0.3	1.0						
Phe.	-0.8	0.5	1.0					
Pyr	0.0	-0.2	-0.3	1.0				
Chry	-0.3	0.5	0.3	0.1	1.0			
Biph	0.4	-0.5	-0.6	-0.3	-0.7	1.0		
Fluo	0.3	-0.7	-0.3	-0.4	-0.7	0.8	1.0	
OTI	-0.3	0.3	0.2	0.5	0.5	-0.7	-0.4	1.0