

APPLICATION OF ISOTOPE-RATIO-MONITORING GAS CHROMATOGRAPHY/MASS SPECTROMETRY TO STUDY CARBONIZATION REACTIONS OF FCCU SLURRY OILS

T. R. Filley, R. M. Filley*, S. Eser*, and K. H. Freeman, Department of Geosciences
*Department of Materials Science and Engineering, The Pennsylvania State University
University Park, PA 16802

ABSTRACT

Delayed coking of Fluid Catalytic Cracking Unit (FCCU) slurry oils produces needle cokes which are used in the manufacture of graphite electrodes for electric-arc furnaces. The structure and properties of needle cokes depend on the formation of a liquid crystalline phase (carbonaceous mesophase) during delayed coking. Thermal reactivity of individual compounds in slurry oils effectively controls the initial carbonization reactions, and, thus, the degree of mesophase development. In this study, isotope-ratio-monitoring gas chromatography mass-spectrometry was used in conjunction with a ^{13}C -labeled dopant (4-methyldibenzothiophene) to determine the distribution of the labeled methyl group on the GC-amenable products from carbonization of three different FCCU slurry oils. Selective removal of the unreacted dopant and its methylated analogs from the reaction products by ligand exchange chromatography allowed the isotope analyses of selected aromatic compounds. The ^{13}C enrichment of selected aromatic compounds, including some isomers, was determined to compare the relative thermal reactivities of different compounds as well as the reactivities of different sites on a given aromatic compound.

INTRODUCTION

The complex chemical constitution of fossil fuels and many associated refinery products precludes the use of simple chromatographic or bulk spectroscopic analytical techniques to accurately evaluate reaction mechanisms and rates of thermal and catalytic conversion of individual compounds. A relatively recent approach to studying the reactivity of individual compounds within complex organic mixtures combines the addition of organic compounds or gaseous media enriched in stable isotopes that participate in alkylation/dealkylation and/or hydrogen abstraction/addition reactions. The rationale for this approach is that the labeled compound or atom can be accurately tracked through a reaction sequence by the use of instrumentation such as, NMR, high resolution mass spectrometry, and isotope-ratio-monitoring gas chromatography mass-spectrometry (irmGCMS). Valuable insights into complex reactions in resid/coal coprocessing¹, crude oil maturation², jet fuel thermal stability³ and the carbonization of FCCU slurry oils^{4,5} have been obtained by this application.

In a previous publication, (Filley et al.⁴), we reported the results from irmGCMS of the reaction products from the carbonization of an FCCU slurry oil (referred to in this paper as Oil A) and 4-methyldibenzothiophene, ^{13}C -labeled at the methyl carbon (4- $^{13}\text{MDBT}$). We observed the progressive ^{13}C -enrichment of methylated PAH within the reaction products during the course of the reaction indicating that ^{13}C -enriched methyl radicals were formed by thermolysis of the labeled methyl group and dibenzothiophene. The reactivity of specific methyl substituted and unsubstituted PAH toward reaction with the ^{13}C -enriched methyl carbon were documented. Filley et al.⁴ observed that the relative enrichment in ^{13}C between structural isomers of specific methyl PAH could be explained based upon calculated reactivities from free valence indices. In this report we present the irmGCMS analysis of the carbonization products of two additional FCCU slurry oils (Oil B and Oil C) with 4- $^{13}\text{MDBT}$ to compare the relative reactivities of specific PAH toward reaction with the ^{13}C -enriched methyl radicals.

EXPERIMENTAL

The FCCU slurry oils were carbonized (500 °C) in closed tubing bomb reactors with 2 wt% 4-methyldibenzothiophene, ^{13}C -labeled at the methyl substituent. Reaction conditions, product extraction and molecular quantification were described in Filley and Eser⁵. The carbon isotopic compositions of individual compounds were determined by isotope-ratio-monitoring gas chromatography-mass spectrometry.⁶⁻⁸ The irmGCMS system used in this study consists of a Varian model 3400 GC coupled to a Finnigan MAT 252 isotope-ratio-monitoring mass spectrometer by a micro-volume combustion furnace. A fused silica capillary chromatographic column (25 m x 0.32 mm i.d. DB-5MS with 0.5 μm film thickness) was used with helium as a carrier gas. As the compounds elute from the gas chromatograph they are catalytically combusted to CO_2 and H_2O within the combustion furnace (Cu:Pt, 2:1 maintained at 850°C). Masses 44 ($^{12}\text{C}^{16}\text{O}_2$), 45 ($^{13}\text{C}^{16}\text{O}_2$, $^{12}\text{C}^{17}\text{O}^{16}\text{O}$) and 46 ($^{12}\text{C}^{18}\text{O}^{16}\text{O}$) are simultaneously monitored. The isotopic compositions of individual compounds were determined by comparison to reference CO_2 gas calibrated relative to NBS-19 standard. Isotopic compositions are reported relative to the international standard, Pee Dee Belemnite (PDB) in delta ($\delta^{13}\text{C}$) notation as described in the following equations.

$$\delta^{13}\text{C}(\text{‰}) = \left[\frac{(R_a - R_n)}{R_n} \right] \times 1000$$

where:

$$R_s = \text{the isotopic ratio } ^{13}\text{C}/^{12}\text{C} \text{ of PDB standard (0.011237)}$$

$$R_m = \text{the isotopic ratio } ^{13}\text{C}/^{12}\text{C} \text{ of the sample compound}$$

The values measured by irmGCMS represent the average isotopic composition of all carbon atoms in the molecule. The ^{13}C -enriched carbon is associated only with the methyl groups on the substituted PAH⁴. Therefore, the isotopic enrichment of the methyl carbons associated with monomethyl substituted PAH was calculated with a mass balance expression. The isotopic enrichment of the methyl group, expressed as $\Delta\delta^{13}\text{C}_m$, is determined by difference between the $\delta^{13}\text{C}$ of the methyl substituent on the methyl PAH produced in the labeled ($\delta^{13}\text{C}_{\text{mL}}$) and unlabeled ($\delta^{13}\text{C}_{\text{mU}}$) experiments. The $\delta^{13}\text{C}_{\text{mL}}$ and $\delta^{13}\text{C}_{\text{mU}}$ cannot be, however, uniquely measured by the technique used in this study, therefore; the $\Delta\delta^{13}\text{C}_m$ is calculated by difference between the measured isotopic composition of a methyl PAH produced during an unlabeled carbonization and the structurally identical methyl PAH produced at 30, 45, and 60 minutes in the ^{13}C labeled carbonization experiments. All enrichments in ^{13}C of alkylated PAH are then reported as the change in isotopic composition of methylated PAH from the unlabeled carbonization experiment. Table 1 gives $\delta^{13}\text{C}$ values of individual compounds in Oil C and the following equations were used to calculate the ^{13}C enrichment of the methyl carbons of a given compound:

$$\Delta\delta^{13}\text{C}_m (\text{‰}) = N_m(\delta^{13}\text{C}_{\text{mL}} - \delta^{13}\text{C}_{\text{mU}}) = N_{\text{mP}}(\delta^{13}\text{C}_{\text{mPL}} - \delta^{13}\text{C}_{\text{mPU}})$$

where:

$\Delta\delta^{13}\text{C}_m$ = Calculated ^{13}C enrichment due to the labeled methyl carbons.

$\delta^{13}\text{C}_{\text{mL}}$ = Isotopic composition of the labeled methyl carbons.

$\delta^{13}\text{C}_{\text{mU}}$ = Isotopic composition of the unlabeled methyl carbons.

$\delta^{13}\text{C}_{\text{mPL}}$ = Measured isotopic composition of the methyl substituted PAH molecule in the labeled experiment

$\delta^{13}\text{C}_{\text{mPU}}$ = Measured isotopic composition of the methyl substituted PAH molecule in the unlabeled experiment.

N_{mP} = Number of carbon atoms in the methyl substituted PAH.

N_m = Number of methyl substituents on the PAH.

For example, consider 1-methylnaphthalene at 45 minutes reaction of Oil C,

$$N_{\text{mP}} = 11$$

$$N_m = 1$$

$$\delta^{13}\text{C}_{\text{mPL}} = 12.7 \text{ ‰}$$

$$\delta^{13}\text{C}_{\text{mPU}} = -27.4 \text{ ‰}$$

$$\Delta\delta^{13}\text{C}_m = 441 \text{ ‰}$$

The high level of ^{13}C enrichment at the methyl carbon becomes evident with this calculation, as illustrated in Table 1 for $\Delta\delta^{13}\text{C}_m$ values for Oil C.

RESULTS AND DISCUSSION

Figure 1 plots the ^{13}C enrichment of specific isomers of monomethyl PAH and pyrene during the course of the reaction for Oil C. All methyl PAH show an increase in isotopic composition with time indicating continual uptake of the ^{13}C -enriched methyl radical. Pyrene, however, does not exhibit any measurable increase in the ^{13}C content. The difference in isotopic composition between methyl substituted and unsubstituted PAH indicates that the ^{13}C -enriched methyl groups do not participate in PAH formation. This behavior was also observed in Filley et al.⁴ for Oil A.

A substantial difference in reactivity is evident between methylpyrenes and methyl-substituted naphthalenes and phenanthrenes where the substituted pyrene compounds consistently demonstrate greater uptake of the labeled methyl group. The greater enrichment of methyl-pyrene is a direct indication of higher reactivity of pyrene in alkylation/dealkylation reactions compared to phenanthrene and naphthalene. The methylphenanthrene and methylnaphthalene isomers overlap in Fig. 1.

There are large differences in reactivity between isomers of methylnaphthalene, methylphenanthrene and methylpyrene. For example, the α positions of 9- and 1-methylphenanthrene are observed to have greater reactivity with respect to the β substituted 3- and 2-methylphenanthrene. Similarly, the α position of 1-methylnaphthalene is more reactive than the β substituted 2-methylnaphthalene. These results are consistent with calculated free valence indices (FVI) of the positions on the unsubstituted PAH which predict greater reactivity at the α positions toward radical attack⁹. Table 2 shows the FVI for each position on the three PAH. Identical relative reactivities were observed for methylPAH in Oil A (Filley et al.⁴) and Oil B. Figure 2 shows the ^{13}C enrichment of 1-methylnaphthalene and 1-methylpyrene for the three oils,

indicating a higher intrinsic reactivity of pyrene compared to that of naphthalene. High reactivity of pyrenes in methylation/demethylation reactions suggests that pyrenes would also be reactive in radical hydrogenation/dehydrogenation reactions. Eser and Jenkins¹⁰ have discussed the significance of hydrogen transfer reactions in controlling the rate of carbonization and fluidity of the carbonizing medium which are critically important for mesophase development. Liu and Eser¹¹ reported that high concentrations of pyrenes in coker feedstocks lead to a high degree of mesophase development, which results in the production of needle cokes with high graphitizability.

The consistent reactivity data obtained from three different feedstocks indicates that the reactivity of individual compounds in FCCU slurry oils can control the initial carbonization chemistry. In other words, the molecular composition of a feedstock can dictate the initial reaction pathways during carbonization, and, thus, control the mesophase development^{5, 11}.

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Table 1. Measured $\delta^{13}\text{C}$ values and calculated ^{13}C enrichment for the methyl group on selected methyl-substituted PAH formed during the carbonization of FCCU slurry oil C with ^{13}C -labeled 4-methyl dibenzothiophene.

Compound	30 min		45 min		60 min	
	$\delta^{13}\text{C}$ (‰)	Δ	$\delta^{13}\text{C}$ (‰)	Δ	$\delta^{13}\text{C}$ (‰)	Δ
2-methylnaphthalene (MN)	-22.0	65	-18.5	103	-13.3	161
1-methylnaphthalene (MN)	-3.7	261	12.7	441	27.6	605
3- and 2-methylphenanthrene (MPh)	-20.0	87	-15.0	162	-5.0	312
9- and 1-methylphenanthrene (MPh)	-7.5	260	6.3	467	14.7	593
Pyrene	-25.1	4.8	-24.7	11	-24.4	16
4-methylpyrene (MPy)	16.4	706	39.5	1098	63.1	1499
1-methylpyrene (MPy)	25.1	869	44.8	1204	74.8	1714

Table 2. Calculated Free Valence Indices of different positions on naphthalene, phenanthrene and pyrene (Coulson, et al.)⁹

	FVI
Naphthalene (position 1)	0.452
Naphthalene (position 2)	0.404
Phenanthrene (position 1)	0.451
Phenanthrene (position 2)	0.402
Phenanthrene (position 3)	0.408
Phenanthrene (position 9)	0.451
Pyrene (position 1)	0.393
Pyrene (position 2)	0.468
Pyrene (position 4)	0.452

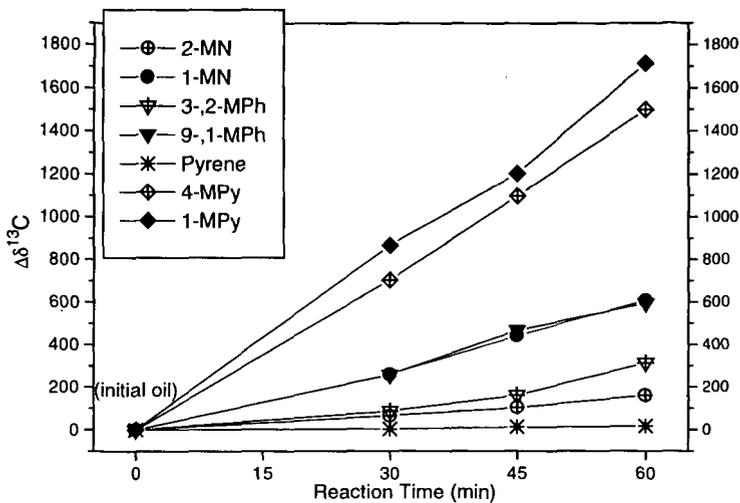


Figure 1. ^{13}C enrichment of the methylsubstituent on selected methylPAH formed during the carbonization of FCCU slurry oil C with ^{13}C -labeled 4-methylthiophene.

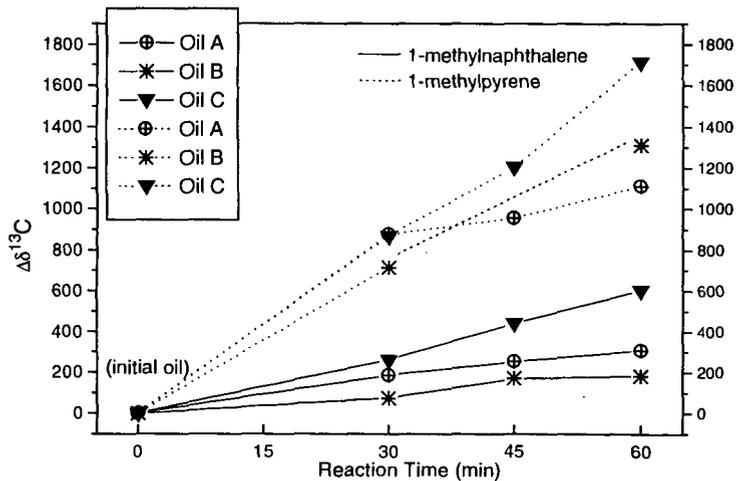


Figure 2. ^{13}C enrichment of the methyl substituent on 1-methylnaphthalene and 1-methylpyrene formed during the carbonization of FCCU slurry Oils A, B, and C with ^{13}C -labeled 4-methylthiophene.