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Molecular Transformation in Hydrotreating Processes Studied by On-Line Liquid Chromatography/Mass Spectrometry

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On-line liquid chromatography/mass spectrometry (LC/MS), in combination with low-voltage electron-impact ionization (LVEI)/medium-resolution mass spectrometry (MRMS, resolution ~10 000) and advanced data analysis procedures, provides us with an opportunity for in-depth molecular level characterization of high-boiling petroleum or synthetic fuel fractions. This combined technique has been applied to the studies of molecular transformation of a petroleum hydrotreating process on different levels: overall changes of hydrocarbons and heteroatom-containing hydrocarbons, compositional changes in terms of compound series, and changes in carbon number distribution within individual compound series. The usefulness of LC/LVEI/MRMS for unraveling some of the complex chemistry associated with heavy hydrocarbon processes has been demonstrated.

INTRODUCTION

Many technical challenges are present in the characterization of high-boiling petroleum fractions due to the complexity of these fractions and limitations in analytical technology.[1] Recent endeavors in combining liquid chromatography and mass spectrometry (LC/MS) enable us to address important science issues and obtain previously unattainable results in petroleum fractions boiling between 650 and 1050 °F. Using a moving-belt interface and low-voltage electron-impact ionization (LVEI) medium-resolution mass spectrometry, on-line LC/MS takes advantage of the unique characteristics associated with LC and MS to differentiate between aromatics and naphthenoaromatics (hydroaromatics) and between aromatic hydrocarbons and hard-to-resolve sulfur compounds. The combination of LC and MS reduces the resolution requirement for accurate mass measurements of aromatic and sulfur compounds.[2]

To effectively process enormous amounts of high-resolution mass spectral data obtained from on-line LC/MS, we developed an innovative data analysis procedure including the use of the Kendrick mass scale (CH_2 = 14.000 000), indigenous mass calibrants, and nominal mass series groupings for the determination of compound type distributions at each LC/MS scan. Higher speed and accuracy than can be obtained by conventional methods are achieved by presorting, grouping, and using statistically averaged mass defects for the determination of the elemental composition of each compound class. Thus, the elution characteristics of individual compound classes within each LC peak can be delineated.[3]

In this paper, we report our studies of molecular transformation occurring in an important petroleum refining process, hydrotreating, using on-line LC/MS operated at LVEI medium-resolution MS mode. As discussed later, hydrotreating greatly alters the molecular composition of the hydrotreated product from its precursor. Our results suggest several reaction pathways taking place in the hydrotreating process. The study demonstrates the roles of on-line LC/MS in the molecular-level understanding of complex chemistry associated with heavy petroleum processes.

EXPERIMENTAL SECTION

A thermally cracked petroleum distillate (8.5% 430–650 °F and 91.5% 650–1050 °F) was hydrotreated at mild conditions to yield a product containing 1.5% naphtha (430 °F), 14.5% 430–650 °C, and 91.6% 650–1050 °F fractions. The 650–1050 °F fractions of the distillate before (containing 2.77 wt % of sulfur and 0.45 wt % of nitrogen) and after (containing 0.34 wt % of sulfur and 0.23 wt % of nitrogen) hydrotreating were subjected to combined LC/MS analysis with instrumental conditions described in our previous paper.[2] In brief, each sample was separated by high-performance liquid chromatography (HPLC) into elution regions of saturates, monoaromatics, diaromatics, triaromatics, tetraaromatics, and polars. An Applied Chromatography Model 750/14 evaporative mass detector (EMD) was used to determine the weight percent of all components in each LC region.[4] The EMD outputs of the distillates before and after hydrotreating are shown in Figure 1. In the LC/MS experiments, the LC eluants were continuously transported into the ion source of a VG-70 VSE double-focusing mass spectrometer by a moving-belt interface. Low-energy electron-impact ionization was used to selectively ionize aromatic hydrocarbons with minimal fragmentation for obtaining the distribution of molecular ions. The resolution of the mass spectrometer was set at 10 000 (medium resolution).

RESULTS AND DISCUSSION

The 650–1050 °F fractions of the thermally cracked distillate before and after hydrotreating were characterized using a moving belt LC/MS. The moving-belt interface is particularly suitable for analysis of 650–1050 °F fractions because the low-boiling fractions are evaporated along with the solvent during sample transport by the belt and high-boiling fractions cannot be completely evaporated by a nose heater located inside the ion source of the mass spectrometer. For fractions with boiling points greater than 1000 °F a different type of LC/MS interface, such as particle beam or thermospray, would be needed to evaporate high-boiling compontents.

Table I compares the overall compound distributions of the distillates before and after hydrotreating, determined by low-voltage electron-impact ionization mass spectrometry (LVEIMS) and an evaporative mass detector (EMD), in each LC elution regions. The LVEIMS values of aromatics and

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(1) Boduszynski, M. M. *Energy Fuels* 1988, 2, 597–612.

(2) Hsu, C. S.; McLean, M. A.; Qian, K.; Aczel, T.; Blum, S. C.; Olmstead, W. N.; Kaplan, L. H.; Robbins, W. K.; Schulz, W. W. *Energy Fuels* 1991, 5, 395–398.

(3) (a) Qian, K.; Chen, Y. C.; Hsu, C. S. *Proceedings of the 39th ASMS Conference on Mass Spectrometry and Allied Topics*, Nashville, TN, May 19–24, 1991; pp 1115–1116. (b) Hsu, C. S.; Qian, K.; Chen, Y. C. *Anal. Chim. Acta* 1992, 264, 79–89.

(4) VanderMeeren, P.; Vanderdeelen, J.; Baret, L. *Anal. Chem.* 1992, 64, 1056–1062 and references cited therein.
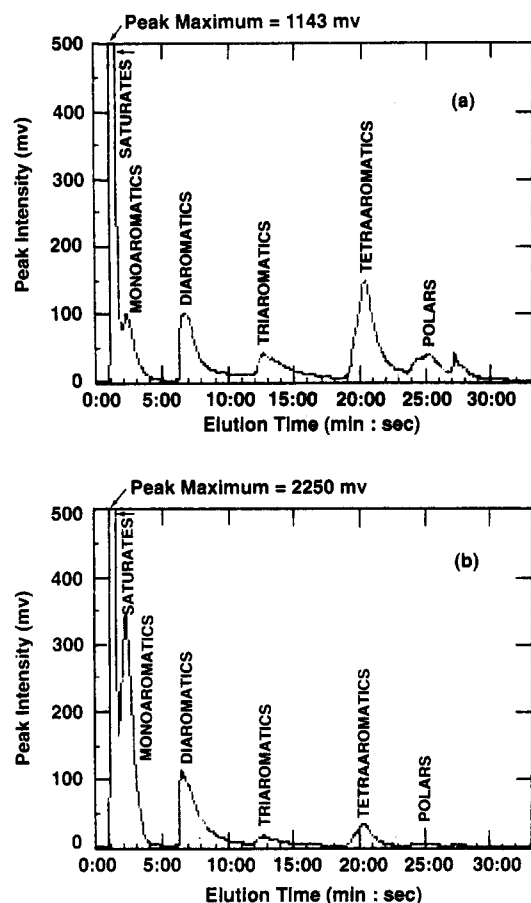
Figure 1. HPLC EMD chromatograms of 650–1050 °F distillates (a) before and (b) after hydrotreating.

Table I. Comparison of Compound Distributions Determined by Low-Voltage Electron-Impact Ionization Mass Spectrometry with Evaporative Mass Detector[a]

LC elution region	before hydrotreating		after hydrotreating	
	EMD	LVEIMS	EMD	LVEIMS
saturates	24.2	(24.2)	36.7	(36.7)
monoaromatics	13.5	12.4	21.9	18.6
diaromatics	13.2	11.5	14.9	15.7
triaromatics	14.8	12.7	11.9	10.0
tetraaromatics	19.4	23.1	9.9	12.3
polars	14.9	16.1	4.7	6.7
total	100.0	100.0	100.0	100.0

[a] Note: The LVEIMS values are normalized to the total of aromatics and polars determined by EMD. The percentage values from EMD are weight percent, while those from LVEIMS are percent of total ionization.

polars shown in the table are normalized to the total of aromatics and polars (excluding saturates) as determined by EMD. The percentage values from EMD are weight percents, while those from LVEIMS are percents of total ionization. The sensitivity of each individual component determined by LVEIMS is dependent on its isomeric structure and molecular weight.[5-10] However, sensitivity measurement of the heavy compounds boiling in the range of 650–1050 °F (mainly

(5) Lumpkin, H. E. *Anal. Chem.* **1958**, *30*, 321–325.

(6) Crable, G. F.; Kearns, G. L.; Norris, M. S. *Anal. Chem.* **1960**, *32*, 13–17.

(7) Lumpkin, H. E.; Aczel, T. *Anal. Chem.* **1964**, *36*, 181–184.

(8) Schulz, J. L.; Sharkey, A. G., Jr.; Brown, R. A. *Anal. Chem.* **1972**, *44*, 1486–1487.

(9) Schiller, J. E. *Anal. Chem.* **1977**, *49*, 1260–1262.

(10) Severin, D.; Deymann, H.; Glinzer, O. *Anal. Chem.* **1982**, *54*, 824–825.

aromatic hydrocarbons and thiophenes) is difficult because very few of the compounds needed for the measurement, especially those which are alkyl substituted and naphthenoaromatic, are available commercially. It is not unreasonable to assume that sensitivities among heavy hydrocarbon isomers are averaged out and almost equal among various compound series (molecular types),[10] thus the percent of ionization can be regarded as weight percent. Table I shows a fairly good agreement in compound distributions determined by LVEIMS and EMD. The LVEIMS values are slightly lower than those of EMD for smaller aromatic cores and higher for more condensed aromatic compounds which have relatively higher ionization cross sections than less condensed aromatic compounds.

Table I also illustrates that upon hydrotreating there was a dramatic increase in monoaromatics accompanied by decreases in tetraaromatics and polars. Some increase in diaromatics and decrease in triaromatics are also observed. The table only represents gross changes in compound distribution observed in the LC separation and does not provide any insight into compositional changes in corresponding LC peaks. As discussed later, a detailed LC/MS analysis revealed upon hydrotreating an increase in naphthenoaromatics and a decrease in heteroatom-containing compounds occur in all of the LC elution regions. The observation of gross changes by LC alone does not unravel the complex chemistry occurring in the hydrotreating process.

Figure 2 exhibits mass spectra integrated over the LC peaks corresponding to monoaromatics, diaromatics, triaromatics, tetraaromatics, and polars (including 4+ ring aromatics) of the distillate before hydrotreating, while Figure 3 shows those after hydrotreating. A general feature of these two figures is that the more polar (or aromatic) the LC region, the lower the average molecular weight. However, direct comparison between the mass spectra of the corresponding LC elution regions before and after hydrotreating is difficult because the hydrotreating process converts compounds in one LC region with their products appearing in another LC region. For example, dibenzothiophenes appear in the triaromatic region before hydrotreating. Their products, biphenyls, are present in the diaromatic region after hydrotreating. It is therefore necessary to analyze these spectra in more detail in order to realize how the molecules transform during the process.

Figures 2 and 3 also show complexity of the spectra. When operated at a medium/high-resolution mode, multiple peaks appear at each nominal mass, resulting in hundreds of mass peaks at each LC/MS scan. To process these enormous amounts of data, we have developed an effective data processing procedure to sort out and group the components in each compound series according to their nominal mass series and Kendrick mass defects and then used the averaged mass defect of the group for the identification of compound series. Thus, this procedure provides a rapid and convenient means of scan-to-scan qualitative and quantitative analysis for the determination of compound series distributions. The elution characteristics of each compound class appearing in the LC peaks can then be delineated.[3]

We used the new procedure outlined above to analyze the mass peaks appearing in Figures 2 and 3 to obtain the distributions of major compound series in the distillate before and after hydrotreating, as illustrated in Figures 4–13. Figures 4–8 exhibit the hydrocarbon series present in the monoaromatic, diaromatic, triaromatic, tetraaromatic, and polar regions of the LC chromatograms, respectively, and Figures 9–13 show the monosulfur compound series present in each of these LC elution regions.
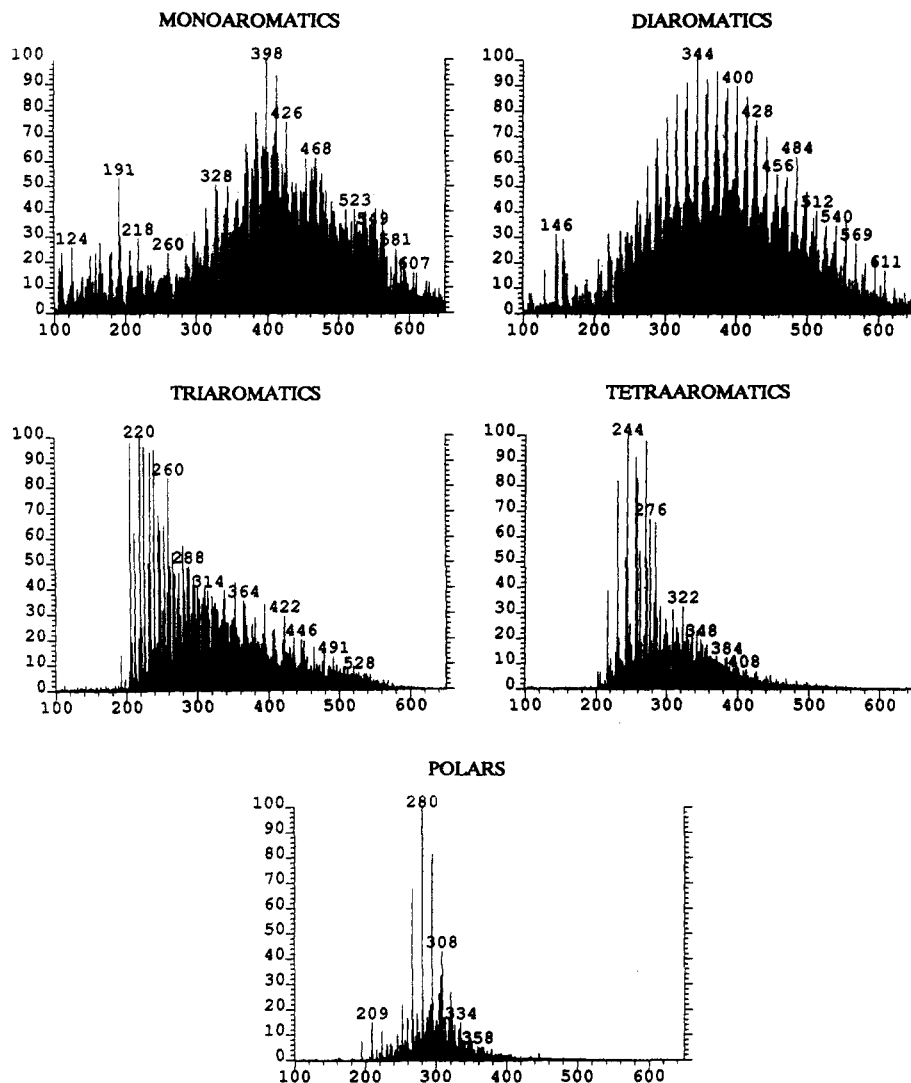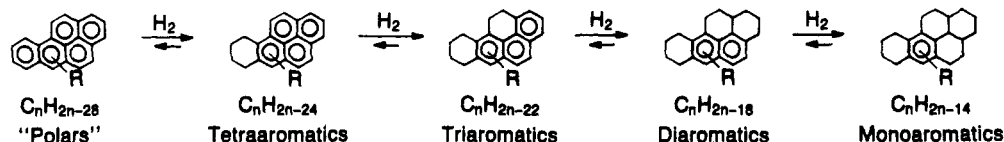
Figure 2. Mass spectra of monoaromatics, diaromatics, triaromatics, tetraaromatics, and polars before hydrotreating.

Scheme I

Let us examine Figure 4 which represents the distribution of compound series in the monoaromatic region before and after hydrotreating. The numbers shown in the abscissa are the z numbers, as in $C_nH_{(2n+z)}X$ where X stands for the heteroatoms (S, N, O, S_2, SO, etc.) in the molecules. In Figure 4, the $z = -6$ series are benzenes. There is a difference between "compound series" and "compound class". A compound series can contain several compound classes. For example the $z = -12$ and -18 series in the monoaromatic region are not naphthalenes, and phenanthrenes; they are actually trinaphthenobenzenes and hexanaphthenobenzenes with typical structures shown in the figure. At this point, we would like to introduce a new nomenclature system for aromatics and naphthenes. The trinaphthenobenzenes contain four rings with only one of them being aromatic; they are denoted as 4R1A. Similarly, hexanaphthenobenzenes, naphthalenes, and perhydrochrysenes are denoted as 7R1A, 2R2A, and 4R0A, respectively. Therefore, the $z = -18$ series in the monoaromatic, diaromatic, and triaromatic regions are 7R1A, 5R2A, and 3R3A, respectively. This coded system would be con-

venient in describing molecular types present in mixtures containing large numbers of hydroaromatics.

In the monoaromatic region, the compound series on the right of the $z = -6$ series are hydroaromatic compounds. Similarly, the compound series on the right of the $z = -12$, -18, $-22/-24$, ..., series in the diaromatic, triaromatic, tetraaromatic, ..., regions are hydroaromatics as well. Although there are no clear cuts in many cases, the suggested boundaries between aromatics and hydroaromatics are indicated in Figures 4–13.

For hydrocarbons as shown in Figures 4–8, compound type distributions change dramatically in the monoaromatic, diaromatic, and triaromatic regions, smaller changes are found in the tetraaromatic and polar regions. Before hydrotreating, the most abundant compound series in the monoaromatic, diaromatic, and triaromatic regions are C_nH_{2n-6} (benzenes, 1R1A), C_nH_{2n-16} (acenaphthenes, dinaphthenonaphthalenes, or vinylbiphenyls; 2R2A), and C_nH_{2n-18} (phenanthrenes, 3R3A), respectively. After hydrotreating, the most abundant series in these regions are C_nH_{2n-14} (tetranaph-
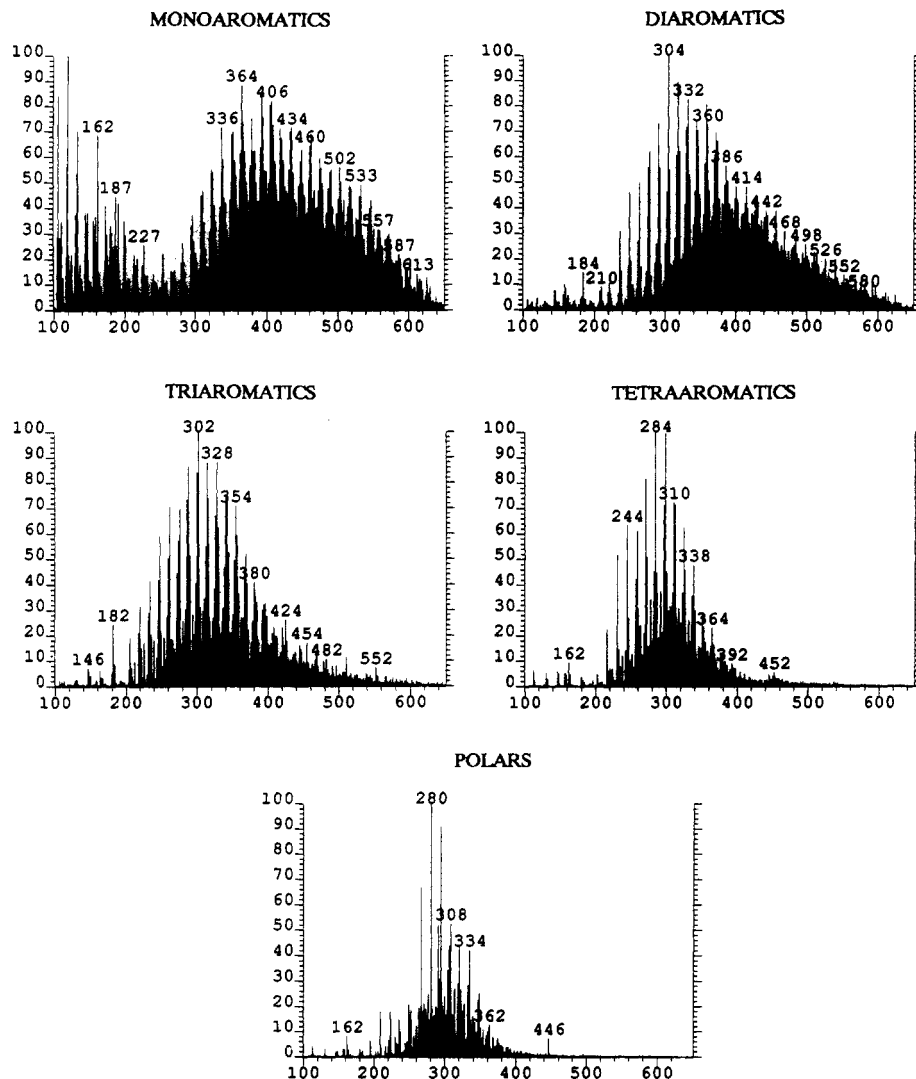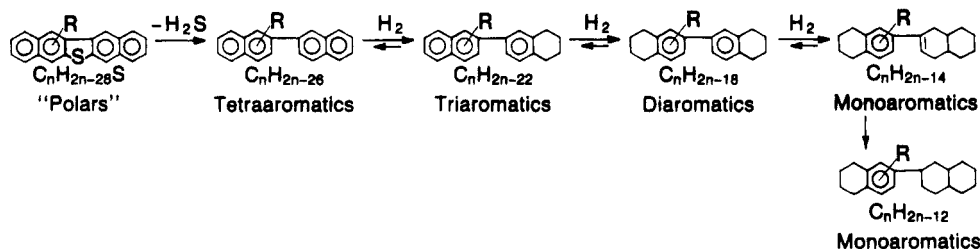
Figure 3. Mass spectra of monoaromatics, diaromatics, triaromatics, tetraaromatics, and polars after hydrotreating.

Scheme II

thenobenzenes, 5R1A), C_nH_{2n-18} (trinaphthenonaphthalenes, 5R2A), and C_nH_{2n-22} (dinaphthenophenanthrenes, 5R3A). These series may contain molecular types representing various degrees of benzopyrene (C_nH_{2n-28}) hydrogenation, shown in Scheme I. Another possible molecular type represented by these series is derived from the hydrogenolysis of dinaphthalenothiophenes and their isomers ($C_nH_{2n-28}S$), shown in Scheme II. Evidently, these simplified schemes do not account for all of the complicated reaction pathways responsible for the molecular transformation in the hydrotreating process. The total decrease in highly condensed aromatic hydrocarbons and thiophenes is less than the total increase in naphthenoaromatics. Some of naphthenoaromatics are possibly formed from cyclization of side chain of alkyl aromatics,[11,12] which can be further hydrogenated to form naphthenoaromatics with larger numbers of naphthenic rings.

With LC/MS, aromatic hydrocarbons and thiophenes with different aromatic ring numbers can be differentiated via the LC ring type[12] separation. However, some ambiguities still exist for resolving overlapping aromatic hydrocarbons from thiophenes that elute in the same LC region.[2] The mass differences between the difficult-to-resolve compound series are typically 3.4 millimass units.[3,13] It would require a mass resolution of over 100 000 to resolve them for compounds in the boiling ranges beyond 650 °F (molecular weights >340). For samples containing rather high concentrations of sulfur compounds, such as the distillate before hydrotreating, the identification of sulfur compounds can be corroborated by

(11) Sullivan, R. F.; Egan, C. J.; Longlois, G. E. J. Catal. 1964, 3, 183–195.

(12) Sullivan, R. F.; Boduszynski, M. M.; Fetzer, J. C. Energy Fuels 1989, 3, 603–612.

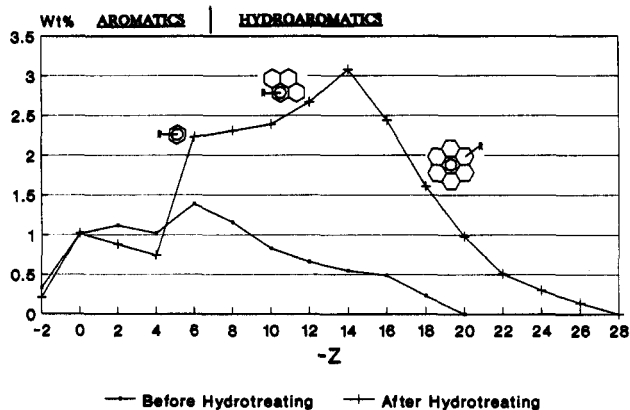(13) Lumpkin, H. E.; Aczel, T. ACS Symp. Ser. 1978, 70, 261–273.

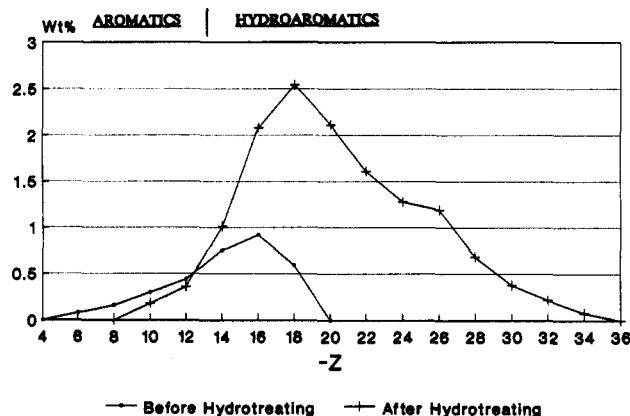**Figure 4.** Distributions of hydrocarbon series in the monoaromatic regions before and after hydrotreating.

Figure 5. Distributions of hydrocarbon series in the diaromatic regions before and after hydrotreating.
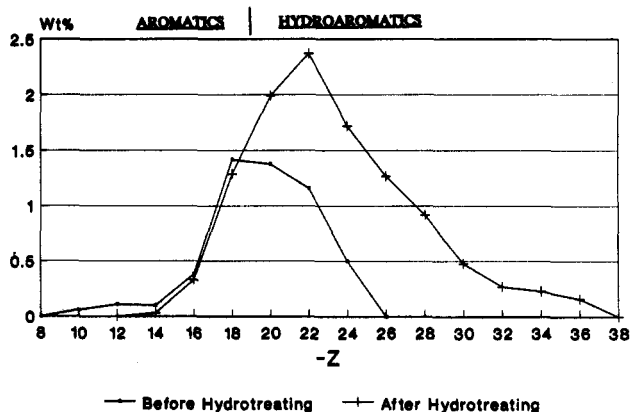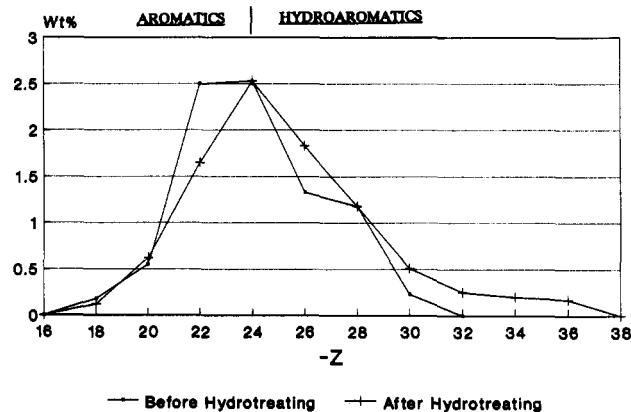

Figure 6. Distributions of hydrocarbon series in the triaromatic regions before and after hydrotreating.

Figure 7. Distributions of hydrocarbon series in the tetraaromatic regions before and after hydrotreating.
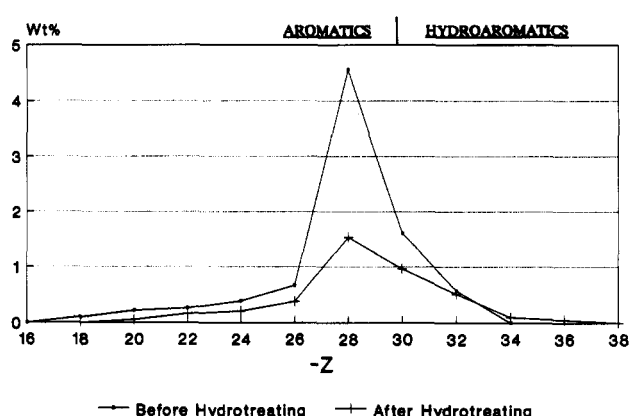

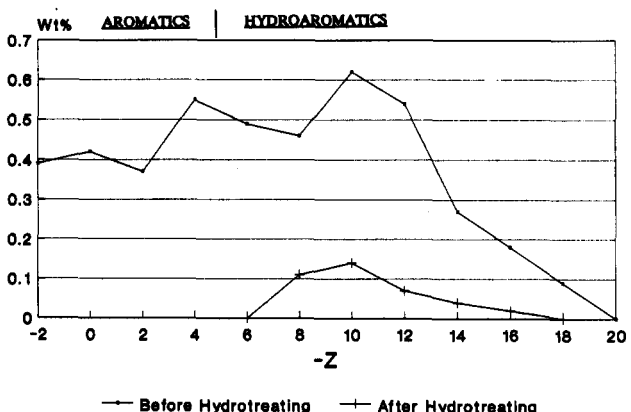**Figure 8.** Distributions of hydrocarbon series in the polar regions before and after hydrotreating.

Figure 9. Distributions of sulfur compound series in the monoaromatic regions before and after hydrotreating.

the use of ^{34}S-containing peaks that are 2 mass units higher than the corresponding compounds of interest.[14] However, for samples containing sulfur compounds in low concentrations, such as hydrotreated distillates, the overlapping compounds can only be resolved by using a high-resolution mass spectrometer with resolving power greater than 100 000 because of the difficulties of detecting insignificant amounts of ^{34}S-containing peaks. Therefore, at 10 000 resolution it is necessary to split the overlapping hydrocarbon and sulfur compound series in the hydrotreated distillate based on the sulfur value determined by elemental analysis.

For the monosulfur compound series shown in Figures 9–13, the major series before hydrotreating are in the diaromatic, triaromatic, and tetraaromatic regions, with the most

(14) Johnson, B. H.; Aczel, T. Anal. Chem. 1967, 39, 682–685.

abundant series in each region to be $C_nH_{2n-10}S$ (benzothiophenes, 2R2A), $C_nH_{2n-16}S$ (dibenzothiophenes, 3R3A), and $C_nH_{2n-22}S$ (benzonaphthalenothiophenes, 4R4A), respectively. Upon hydrotreating, all of the monosulfur series are reduced in significant amounts. Thiophenes are more effectively removed than naphthenothiophenes. For example, the $C_nH_{2n-16}S$ series (dibenzothiophenes) is reduced in a larger extent than the $C_nH_{2n-18}S$ (naphthenodibenzothiophenes, 4R3A) and $C_nH_{2n-20}S$ (dinaphthenodibenzothiophenes, 5R3A) series.

The carbon number distribution of each compound series can also be studied in great detail. Figures 14 and 15 show the carbon number distribution for the C_nH_{2n-18} (phenanthrenes) and $C_nH_{2n-16}S$ (dibenzothiophenes) in the triaromatic region. The distribution of phenanthrenes maximizes at C_{17} and C_{18} (C_3- and C_4-substituted) before hydrotreating,
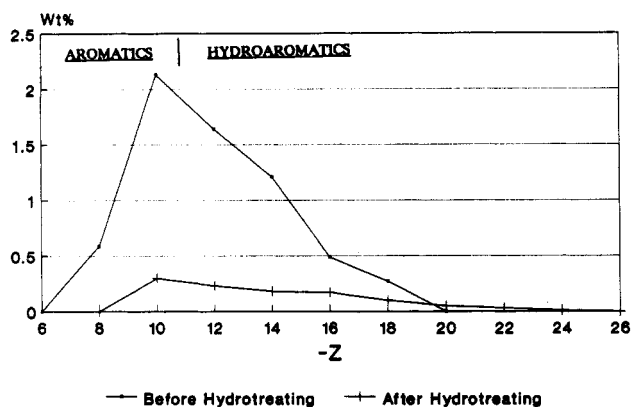
Figure 10. Distributions of sulfur compound series in the diaromatic regions before and after hydrotreating.
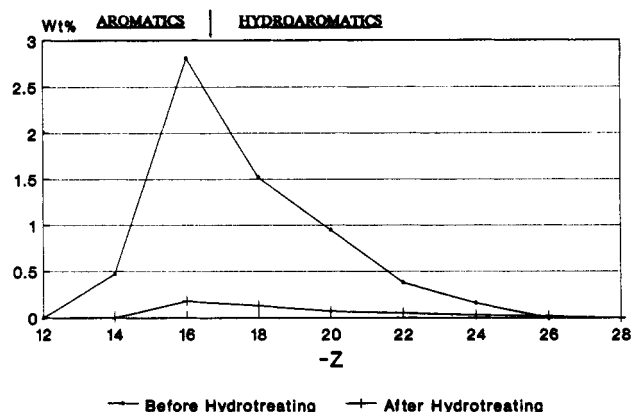

Figure 11. Distributions of sulfur compound series in the triaromatic regions before and after hydrotreating.

but at C_{20} and C_{21} (C_6- and C_7-substituted) after hydrotreating. This indicates that the least-substituted and shortest side chain phenanthrenes are most effectively converted into hydrophenanthrenes. The additional C_{20} and C_{21} phenanthrenes after hydrotreating come from many different sources, such as hydrogenolysis of phenanthrenethiophenes and hydrogenation of aromatics followed by ring opening:
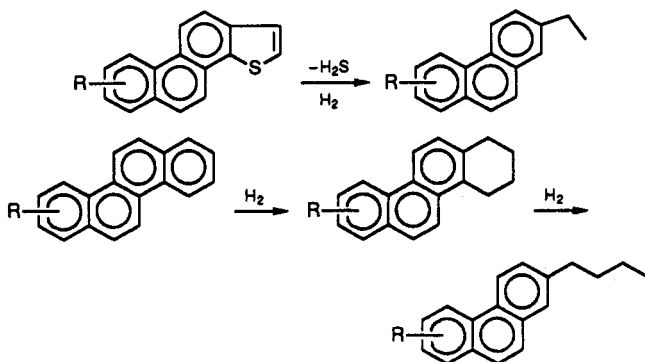
In the $C_nH_{2n-16}S$ series, more effective removal of dibenzothiophenes occurs among lower members of the series that have low alkyl substituents. The less effective removal of dibenzothiophenes with higher carbon numbers is possibly due to the presence of more isomers with steric hindrance around the sulfur center. The sterically hindered thiophenes are known to be refractory to hydrodesulfurization and referred to as "hard" sulfur compounds. In both C_nH_{2n-18} and $C_nH_{2n-16}S$ series, there is no evidence of hydrocracking from the carbon number distributions observed before and after the hydroprocessing. In fact, the average carbon number is shifted to a higher rather than a lower value after hydro-
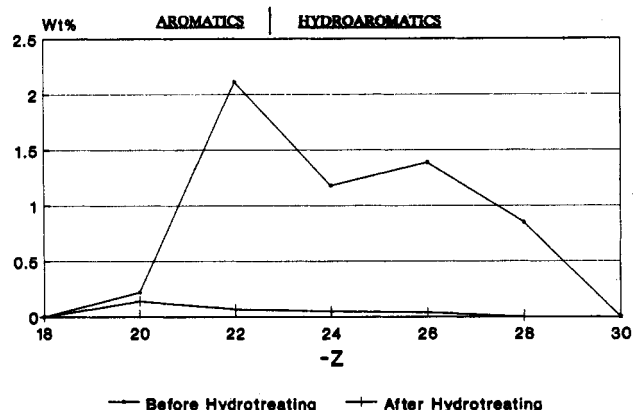

Figure 12. Distributions of sulfur compound series in the tetraaromatic regions before and after hydrotreating.
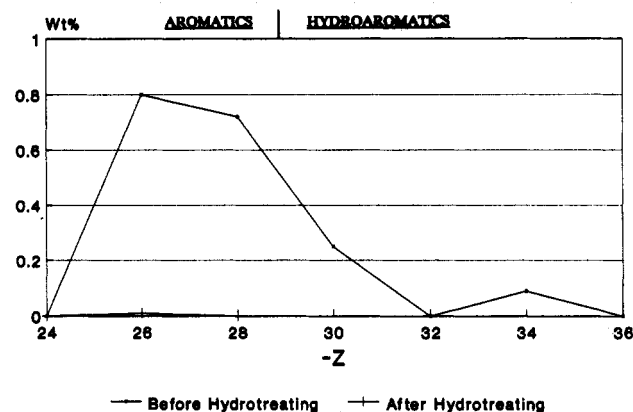

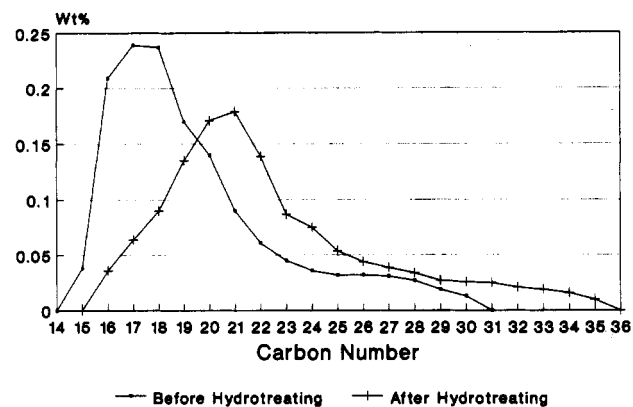**Figure 13.** Distributions of sulfur compounds series in the polar regions before and after hydrotreating.

Figure 14. Carbon number distributions of the C_nH_{2n-18} (phenanthrenes) series in the triaromatic region before and after hydrotreating.
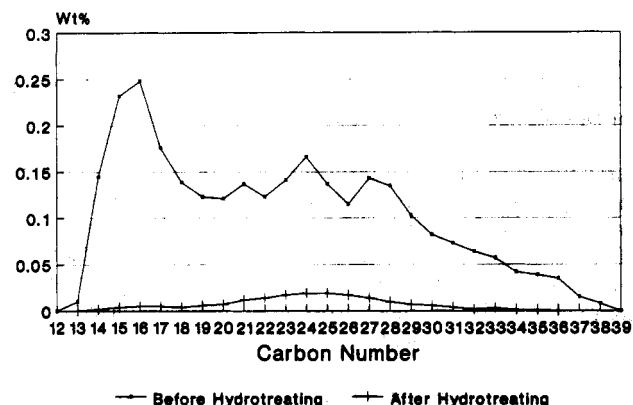

Figure 15. Carbon number distributions of the $C_nH_{2n-16}S$ (dibenzothiophenes) series in the triaromatic region before and after hydrotreating.

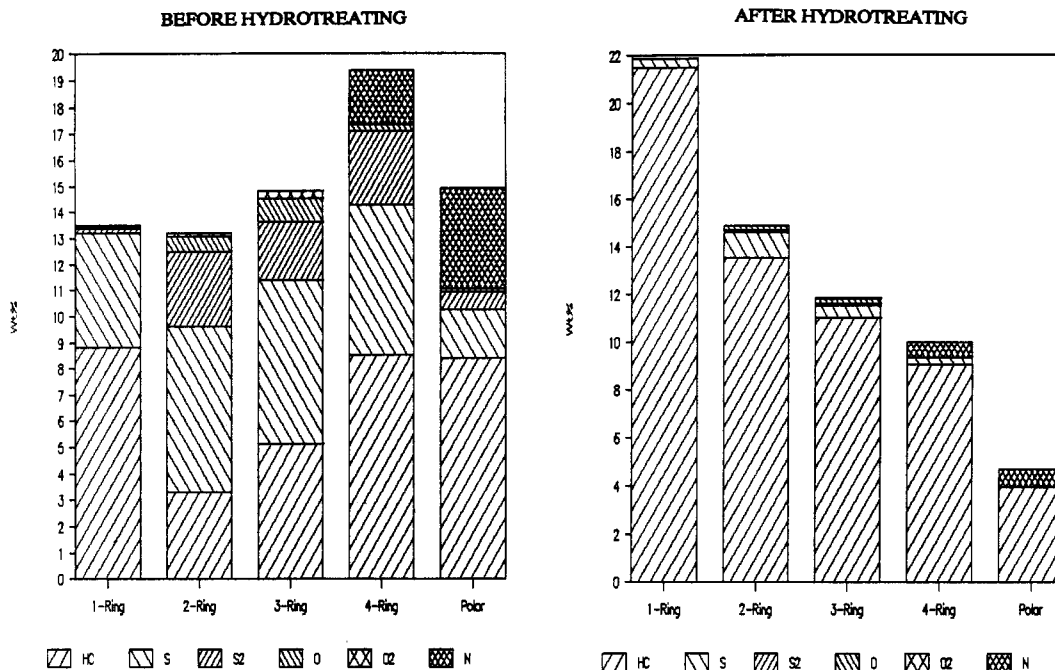BEFORE HYDROTREATING   AFTER HYDROTREATING

Figure 16. Overall compound type distributions of the distillate in each LC aromatic ring regions before and after hydrotreating.

treating. This is reasonable considering the short side chain nature of thermally cracked distillates and mild hydrotreating conditions used. On the other hand, hydrocracking is an important refining process for residuum-derived vacuum gas oils (VGO's) that are rich in aromatic compounds with long alkyl substituents.[13]

The overall compositional changes in the LC aromatic ring regions of the distillate before and after hydrotreating can be summarized in Figure 16. The relative abundances of different compound types are normalized to the largest LC peaks (in peak area) found in each sample. Six compounds types, i.e., hydrocarbons, monosulfur, disulfur, monooxygen, dioxygen, and mononitrogen, are identified in the thermally cracked petroleum distillate. As intended, the hydrotreating substantially reduces the amounts of monosulfur compounds in all LC regions, accompanied by a large increase in the amounts of hydroaromatic hydrocarbons. The other heterocompounds in the feed are more narrowly distributed with oxygen compounds mostly in the diaromatic and triaromatic regions and nitrogen compounds abundant in the tetraaromatic and polar regions. Further studies showed that the nitrogen compounds are mainly 5-membered nitrogen heterocyclics (pyrrolic nitrogen compounds, such as carbazoles) and 6-membered nitrogen heterocyclics (basic nitrogen compounds, such as quinolines) with the z-distributions ranging from $-15N$ to $-27N$. Upon hydrotreating, most of the hydroaromatic hydrocarbons formed are in the monoaromatic and diaromatic regions. Disulfur and oxygenated compounds are almost completely removed, while certain amounts of monosulfur and nitrogen compounds survive from hydrotreating. Disulfur compounds appear to contain external thiophene rings which are less sterically hindered and more susceptible to hydrogenolysis than monosulfur compounds. Partial conversion of disulfur compounds could account for some of the monosulfur compounds remaining after hydrotreating.

CONCLUSION

On-line LC/MS in combination with low-voltage EI/medium-resolutions MS provides us with an unprecedented opportunity for the in-depth molecular level characterization of high-boiling petroleum or synthetic fuel fractions without the need of using high-resolution mass spectrometry. With an advanced data analysis procedure to process medium/high-resolution data, the compositional changes within each LC peak can be studied in great detail. This combined technique has been applied to study molecular transformation of a hydrotreating process on different levels: (1) overall changes of hydrocarbons and heterocompounds, (2) compositional changes in terms of compound series, and (3) changes in carbon number distribution of individual compound series. The combination of LC and MS enhances either technique to obtain previously unattainable results in the characterization of heavy hydroaromatics and heteroaromatics, thus demonstrating the value of on-line LC/MS for detailed molecular transformation studies to unravel complex chemistry associated with heavy hydrocarbons refining processes.

ACKNOWLEDGMENT