Compositional Characterization of Petroleum Heavy Oils Generated from Vacuum Distillation and Catalytic Cracking by Positive-mode APPI FT-ICR Mass Spectrometry

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Abstract: Molecular compositions of two types of heavy oil were studied using positive atmospheric pressure photoionization (APPI) Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). Vacuum gas oil (VGO) was generated from vacuum distillation of atmospheric residual oil (AR), and slurry oil (SLO) was generated from catalytic cracking of AR. These heavy oils have similar boiling point ranges in the range of 210-650°C, but they showed different mass ranges and double-bond equivalent (DBE) distributions. Using DBE and carbon number distributions, aromatic ring distributions, and the extent of alkyl side chains were estimated. In addition to the main aromatic hydrocarbon compounds, those containing sulfur, nitrogen, and oxygen heteroatoms were identified using simple sample preparation and ultra-high mass resolution FT-ICR MS analysis. VGO is primarily composed of mono- and di-aromatic hydrocarbons as well as sulfur-containing hydrocarbons, whereas SLO contained mainly polyaromatic hydrocarbons and sulfur-containing hydrocarbons. Both heavy oils contain polyaromatic nitrogen components. SLO inludes shorter aromatic alkyl side chains than VGO. This study demonstrates that APPI FT-ICR MS is useful for molecular composition characterization of petroleum heavy oils obtained from different refining processes.

Key words: Vacuum gas oil, Slurry oil, FT-ICR MS, APPI, Petroleum, Heavy oil.

Introduction

Due to increasing crude oil prices and the availability of sour heavy crude oils and unconventional crude oils, most refineries are trying to upgrade the residual heavy oil fractions of petroleum to transportation fuels or petrochemicals to maximize profits from crude oil. Compositional information on residual heavy oils is useful for developing such upgrading processes and catalysts. Heavy oil composition studies are also useful for crude oil evaluation and process optimization.

Petroleum is one of the most complex natural mixtures. Crude oils can be distillated and fractionated through atmospheric pressure distillation into C3-C4 gases, naphtha, kerosene, light gas oil (LGO), and atmospheric residual oil (AR). Table 1 shows the approximate boiling ranges of each fraction. AR can be divided into vacuum gas oil (VGO) and vacuum residual oil (VR) through vacuum distillation. Residual oils, like AR and VR, contain asphaltenes, which can cause deposition or coking problems. The molecular compositions of gases and gas oil can be analyzed using commercial one-dimensional gas chromatography (ASTM D2163, D6296, D6730, D6733, D6968) or two-dimensional gas chromatography.[1-3] For

Table 1. Typical boiling point ranges of distilled fractions of crude oils by atmospheric pressure distillation.

Distilled Fraction	Boiling Range (°C)
LPG	~25
Naphtha	25~170
Kerosene	150~270
Light gas oil	250~380
AR	380~

component analysis of heavy oils at the molecular level, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) has proven useful because of its the ultra-high mass resolution power, greater than several hundreds of thousands of Daltons.[4-6]

For petroleum analysis by FT-ICR MS, several ionization methods, such as electrospray ionization (ESI), atmospheric pressure photoionization (APPI), and atmospheric pressure chemical ionization (APCI), can be used. Heavy oils, like VGO, deasphalted oil (DSO), AR, and asphaltenes, and process deposits, have been analyzed by ESI[15-18] and APPI.[19-21] Positive-mode APPI and APCI can be used for aromatic compounds, compounds containing one or two sulfur atoms, and nitrogen compounds.[7-11] Negative-mode APPI and ESI can be used

for naphthenic acids and non-basic nitrogen compounds.[12-14] Heteroatom compounds like sulfur, nitrogen, naphthenic acids, and metal porphyrins in petroleum heavy oils need to be removed prior to upgrading, because they will poison the catalyst. Heteroatom components in crude oils or heavy oils can be analyzed with FT-ICR MS using simple sample preparation.

In this work, two types of heavy oil from different refinery processes were compared by 7T FT-ICR MS coupled with APPI : VGO and slurry oil (SLO). SLO is the bottom oil after catalytic cracking of AR. The two heavy oils have similar boiling point ranges and the same order of nitrogen and sulfur contents. Carbon number distribution, core molecular aromatic structure, and the primary heteroatom components were compared. This work demonstrated the usefulness and practicality of APPI FT-ICR MS for heavy oil component characterization and refinery research.

Experimental

VGO and SLO samples were provided by the Energy Process Laboratory, SK Innovation. Table 2 shows the boiling point distributions and sulfur and nitrogen contents of the two samples. Samples were dissolved in toluene at 0.05 wt% (high-performance liquid chromatography (HPLC)-grade toluene was used without further purification). Toluene is commonly used as dopant for improving efficiency of photoionization. Diluted samples were injected directly using a syringe pump at a flow rate of 300 µL/h. Analyses were performed using a 7T FT-ICR mass spectrometer attached to an APPI source obtained from Bruker Daltonics (Billerica, MA). Nitrogen was used as the drying and nebulizing gas for the ionization source. For APPI analysis, the nebulizing temperature was set to 350 °C, with a flow rate of 3.0 L/min, and the drying gas temperature was set to 200 °C, with a flow rate of 2.0 L/min. Ionized samples were accumulated in the collision cell for 0.2 s and transferred to the ion cyclotron resonance (ICR) cell with a 2-ms time-of-flight window. The ions were trapped in the ICR cell with a sidekick voltage of 8 V. At least 100 scans were accumulated to increase the signal-to-noise ratio. In total, 2×10^6 data points were recorded. An average resolving power of 295,000 at *m/z* 200-800 was routinely observed.

Spectral interpretation was performed using the ChemBrowser

Table 2. Bulk properties of VGO and SLO.

	VGO	SLO
Boiling point, °C		
0.5% Distilled	260	215
50% Distilled	455	425
90% Distilled	560	540
99.5% Distilled	650	605
Sulfur, wt%	3.50	1.00
Nitrogen, wt%	0.20	0.25

software (BNF Technology Inc., South Korea). The threshold for peak-picking was a signal-to-noise ratio higher than 4.5. After peak-peaking and internal calibration, molecular formulae were assigned within a 2-ppm error range.

Results and Discussion

Mass Spectra and Compound Classes Observed by Positive APPI

Figure 1 shows positive APPI FT-ICR mass spectra of the two heavy oil samples. The average resolution of the full-width at half-maximum (FWHM) peak height was almost 295,000 between *m/z* 200 and 800. The mass range of VGO was from 250 to 700 Da and that of SLO was from 200 to 550 Da. The average masses of VGO and SLO were 440 and 362 Da, respectively. The average mass was calculated using the following equation,

$$Average\ Mass = \frac{\sum_i M_i I_i}{\sum_i I_i} \tag{1}$$

where M_i is the mass of peak i, and I_i is the relative intensity of peak i.

The spectra were calibrated using internal CH_2 series peaks of DBE 4 HC class compounds, and the molecular formulas were assigned within an error of 2 ppm. Figure 2 shows the compound class distribution, ionized by positive photoionization. The main component classes observed by positive APPI were hydrocarbon, S1 (components containing one sulfur atom), N1, and S2. Because VGO contained three times more sulfur than SLO, S1 and S2 compounds were more abundant in VGO than in SLO. Additionally, the relative abundance of hydrocarbons was lower in VGO than in SLO. The characteristics of each compound class were compared
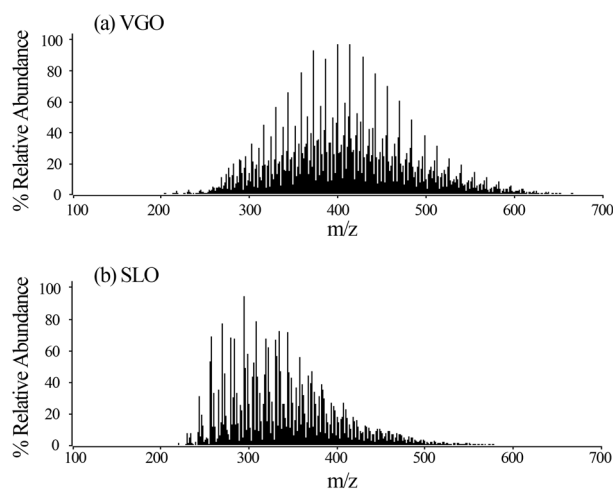

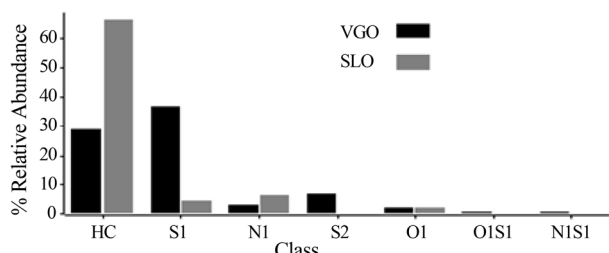**Figure 1**. Positive-mode APPI FT-ICR mass spectra of (a) VGO and (b) SLO.

Figure 2. Class distributions observed by positive-mode APPI FT-ICR MS.

in more detail, as discussed in the following section.

Aromatic Hydrocarbon Compounds

Using molecular formula data obtained by ChemBrowser software, the double bond equivalents (DBEs), carbon numbers, and the extent of alkylation were determined. DBE is the sum of the number of rings and double bonds calculated from the molecular formula [22]:

$$DBE = c - \frac{1}{2}h + \frac{1}{2}n + a \quad (\text{for } C_cH_hN_nO_oS_s) \tag{2}$$

Figure 3 shows the relative abundance distribution of the hydrocarbon class (HC) as a function of DBE and carbon number. The average carbon numbers of VGO and SLO were 32.4 and 27.9, respectively. The average DBEs of VGO and SLO were 8.5 and 15.4, respectively. The average carbon numbers and average DBEs were calculated using equations similar to equation (1). The content of the non-aromatic fraction of VGO and SLO determined by open column chromatography was about 50 wt% and 80 wt% respectively. Non-aromatic compounds have DBE values between 0 and 3 because a benzene ring has a DBE value of 4. The relative intensity of compounds with DBE values between 0 and 3 observed by APPI FT-ICR MS was relatively low, suggesting that non-aromatic hydrocarbons were not ionized by APPI. APPI is useful for characterization of aromatic compounds of petroleum. The molecular composition of aromatic compounds of petroleum is important for evaluation of fuel quality or hydroprocessing study. The DBEs of benzene, naphthalene, and anthracene were 4, 7, and 10, respectively, but the DBEs of the hydrocarbons in VGO were primarily 4-10. This suggests that the aromatic hydrocarbons were primarily mono- or di-aromatic. For SLO, most hydrocarbon DBEs were greater than 10. Thus, the aromatic hydrocarbons of SLO were composed primarily of polyaromatics with more than three benzene rings.

The length of the alkyl chains attached to the core aromatic group can be estimated from the carbon number distributions. A higher carbon number with the same DBE value means that longer alkyl chains are attached to the core aromatic group. The carbon number distributions at each DBE value for VGO were wider and higher than those of SLO, suggesting that VGO contained more alkyl side chains than SLO.

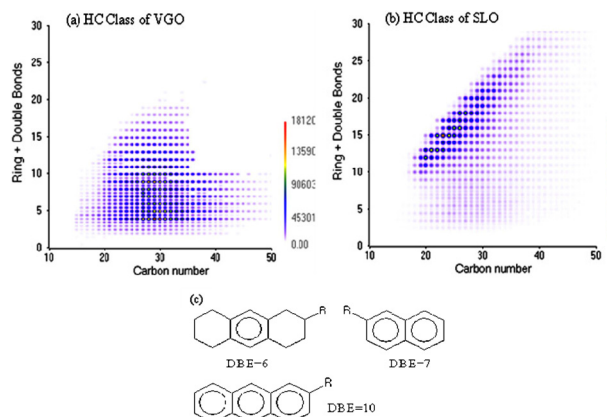VGO contained primarily mono- or di-aromatic hydrocarbons

Figure 3. DBE and carbon number distributions of hydrocarbon classes in (a) VGO and (b) SLO and (c) suggested structures of aromatic HC compounds, based on their DBE values.
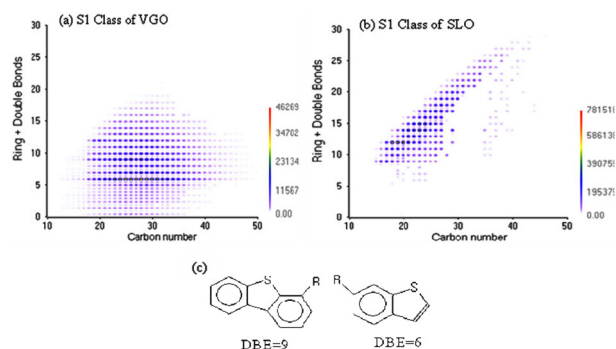

Figure 4. DBE and carbon number distributions of the S1 class in (a) VGO and (b) SLO and (c) suggested structures of S1 compounds, based on their DBE values.

rather than polyaromatics, and the aromatic hydrocarbons contained longer or a greater number of alkyl side chains than those of SLO. SLO contained primarily polyaromatic hydrocarbons and had shorter alkyl side chains. The structural differences observed in this study are consistent with expectations for the samples and are reasonable because SLO was generated by catalytic cracking. Through the cracking process, the alkyl side chains were cracked into gases or lighter compounds.

Sulfur- and Nitrogen-Containing Compounds

The DBE and carbon number relative abundance distributions of the S1 class of VGO and SLO are shown in Figure 4. The DBE of benzothiophene was 6, and the DBE of dibenzothiophene was 9. The S1 class of VGO showed a relatively high abundance, from DBE 6 to 12, but most of the DBE values of the S1 class of SLO were greater than 9. From the DBE distribution of the S1 class, we concluded that VGO contained primarily mono- or di- aromatic sulfur compounds, and most of the S1 class compounds of SLO were polyaromatics. The carbon number distribution of the S1 class of VGO was higher than that of SLO. Similar to the aromatic hydrocarbon class, the S1 class of VGO had more alkyl side chains than that of SLO.
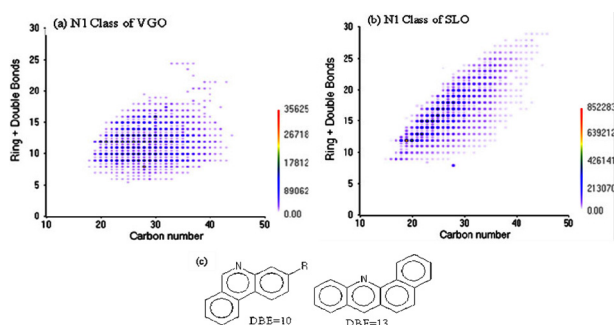
Figure 5. DBE and carbon number distributions of the N1 class observed in (a) VGO and (b) SLO and (c) suggested structures of N1 compounds, based on their DBE values.

Because the results for the S2 class were the same as those for the S1 class, the data are not shown in this paper.

Figure 5 shows the DBE and carbon number distributions of the N1 class. The N1 class of VGO had DBE values greater than 7, and most were greater than 10. From the DBE values of the N1 class, we concluded that the primary components of the N1 class were polyaromatics, such as acridine and its derivatives.

Conclusions

The molecular compositions of two types of petroleum heavy oils were studied using FT-ICR MS coupled with atmospheric photoionization. From DBE and carbon number distributions, the core structure of aromatic hydrocarbons and heteroatom compounds and the extent of alkyl side chains were estimated. Vacuum-distilled heavy oil contained more mono- and di- aromatics and longer alkyl side chains than those that were catalytically cracked. The catalytically cracked heavy oil contained polyaromatics and shorter alkyl side chains. In the future, information on the content of naphthenic rings and the length of alkyl side chains obtained using other analytical methods will be compared with the results obtained by FT-ICR MS.

Acknowledgments

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