Nitrogen Compounds Characterization by High Resolution MS

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Characterization of Basic Nitrogen-Containing Compounds in the Products of Lube Base Oil Processing by Electrospray Ionization Fourier Transform Ion Cyclotron Resonance Mass Spectrometry

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The distribution of basic nitrogen-containing compounds in three vacuum gas oils (VGOs) with different boiling ranges and their dewaxed oils from the lube base oil refining unit of a refinery were characterized by positive-ion electrospray ionization (ESI) Fourier transform-ion cyclotron resonance mass spectrometry (FT-ICR MS). It turned out that the composition of basic nitrogen compounds in the samples varied significantly in DBE and carbon number, and the dominant basic N-containing compounds in these oil samples were N_1 class species. N_1O_1, N_1O_2, and N_2 class species with much lower relative abundance were also identified. The composition of basic nitrogen compounds in VGOs and dewaxed VGOs were correlated with increased boiling point and varied in DBE and carbon numbers. The comparison of the analytical results between VGOs and dewaxed VGOs indicated that more basic N-containing compounds in VGO with low carbon number and small molecular weight tend to be removed by solvent refining in lube base oil processing.

Key Words : Basic nitrogen compounds, Lube base oil processing, ESI FT-ICR MS

Introduction

Nitrogen-containing compounds in petroleum contain both neutral and basic nitrogen compounds. Neutral nitrogen compounds accounting for less than 30% of all organic nitrogen compounds include carbazoles, indoles, and pyrroles *etc.* Basic nitrogen compounds include, for example, pyridine and quinoline derivatives.[1] They are problematic in refining processes because they lead to catalyst deactivation and cause fuel instability during transportation or storage.[13] Nitrogen compounds tend to exist in the higher boiling fractions and residues.[4] Among the refinery product streams, vacuum gas oil (VGO) is known to contain a considerable percentage of the total nitrogen compounds, which is only preceded by vacuum residue (VR).

Gas chromatography (GC) and GC coupled with mass spectrometry (GC-MS) were commonly used to characterize the nitrogen compounds in crude oil and its distillates. However, GC-MS is not capable of analyzing samples that contain higher molecular-mass nitrogen compounds because of their low volatility.[2,5] Recently, Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS) with an ultrahigh mass resolution and mass accuracy has been successfully used to analyze trace polar compounds found in petroleum systems at the molecular level. Positive-ion ESI can selectively ionize heteroatom species, such as basic nitrogen compounds, and negative-ion ESI can be used for acids and neutral nitrogen compounds.[2,6,7] Smith *et al.*[8] analyzed the polar heteroatom species including basic and neutral nitrogen compounds in eight heavy vacuum gas oil (HVGO) distillation fractions with different boiling ranges

of Athabasca bitumen by positive- and negative-mode ESI FT-ICR MS. Liu *et al.*[4] has characterized the composition of basic nitrogen compounds in the products of Liaohe atmospheric residue hydrocracking including VGOs by positive-ion ESI coupled with FT-ICR MS.

The majority of lubricant base oils are produced by refining crude oil. The solvent dewaxing process is used as a conventional and important technique for the removal of wax from VGO in the temperature range of the desired pour point, and followed by another solvent extraction process to remove undesirable components such as aromatics and other materials low viscosity index.[9] After the two sequences of refining techniques to VGO, the dewaxed VGO as the candidate of lube base oil is obtained. We have utilized negative-ion ESI FT-ICR MS to obtain detailed molecular compositions of acidic compounds in three different boiling point VGO samples and their corresponding dewaxed VGOs, and found that N_1 class species of carbazoles and benzocarbazoles with DBE (double bond equivalent) values of 9 and 12 were dominant in three VGOs, and N_1 class species with a DBE of 9 were dominant in their dewaxed VGOs after the lube base oil refining process.[10]

In the present work, the classes and structures of basic nitrogen species in three VGOs and the corresponding dewaxed VGOs collected from a refinery in China were characterized by using the 9.4 T ESI FT-ICR MS. The detailed information about compositional changes of basic nitrogen compounds from molecular level in lube base oil processing was determined for better understanding to the process, which can be useful in the designing and developing of the technologies for refining base oil.

Experimental

Materials. Three VGO samples and their dewaxed oils used in the experiments were collected from no. 3 refinery of the Yanshan Petrochemical Company of SINOPEC, the physicochemical properties are presented in Table 1. The VGO samples from the vacuum distillation unit were cut-2, cut-3, and cut-4 with the boiling ranges of 360-400 °C, 400-450 °C, 450-490 °C, respectively. It can be seen that the basic nitrogen content was decreased after refining, and the removal efficiency reduced from cut-2 to cut-4. So the further denitrification processes, such as using complexing agents and clay adsorbents, are necessary to meet the related requirement of basic nitrogen content in lube base oil.

ESI FT-ICR MS Analysis. The VGOs and dewaxed VGOs were analyzed by Bruker apex-ultra FT-ICR MS equipped with a 9.4 T superconducting magnet. Sample preparation method by positive-ion ESI FT-ICR MS has been previously reported.[2,5] The sample solution was infused *via* an Apollo II electrospray source at 180 μL/h by a syringe pump. The operating conditions for positive-ion formation were −4.0 kV emitter voltage, −4.5 kV capillary column front end voltage, and 320 V capillary column end voltage. Ions accumulated for 0.01 s in a hexapole with 2.4 V direct current voltages and 200 V_{pp} radio frequency (RF) amplitudes. The delay was set to 1.2 ms to transfer ions to an ICR cell by the electrostatic focusing of transfer optics. The mass range was set at *m/z* 150-800. The data size was set to 4 M words, and time-domain data sets were co-added from 128 data acquisitions.

Mass Calibration and Data Analysis. The mass spectra obtained were calibrated internally according to the most

Table 1. Properties of the VGOs and dewaxed VGOs

Sample	Density at 20 °C, kg/m³	Dynamic viscosity, mm²/s		Basic nitrogen, μg/g oil
		40 °C	100 °C	
VGO-2	856.5	15.4	4.6	164
VGO-3	873.9	34.1	6.5	241
VGO-4	881.4	74.6	11.1	412
De-waxed VGO-2	872.6	30.4	5.1	69
De-waxed VGO-3	886.0	66.9	8.0	108
De-waxed VGO-4	886.4	127.3	12.6	252

abundant homologous series N-containing compounds. Peaks with relative abundance greater than 6 times the standard deviation of the baseline noise level were exported to a spreadsheet. Data analysis was implemented by using custom software which had been described by some references.[11,12] In general, the data analysis was performed by selecting a two-mass scale-expanded segment in the middle of the mass spectrum, followed by detailed identification of each peak. The peak of at least one of each heteroatom class species was arbitrarily selected as the reference. Compounds of a homologous series would be identified according to the Kendrick mass defect (KMD), and the essence was that compounds with the same heteroatom composition and number of rings plus double bonds (DBE). DBE was defined as the number of rings plus double bonds involving carbon for a petrochemical of composition.[13]

Results and Discussion

Heteroatom Class Distribution in the VGOs and de-
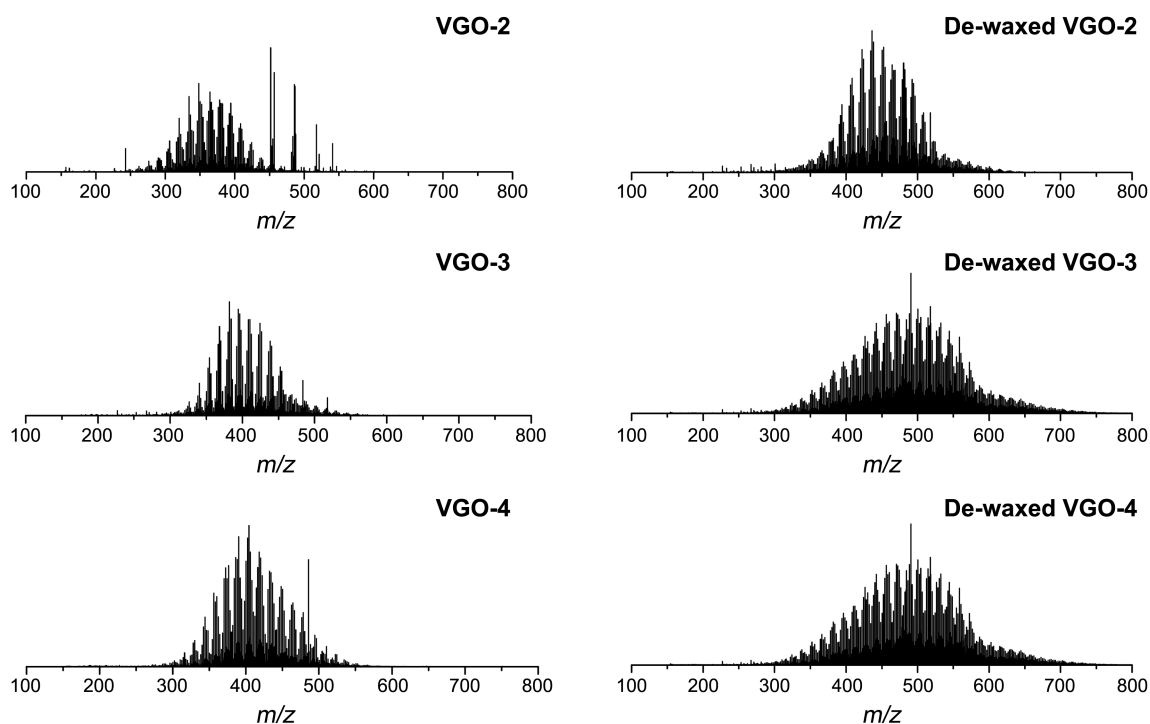
Figure 1. Mass spectra of the VGO cuts and their dewaxed oils from positive-ion ESI FT-ICR MS.
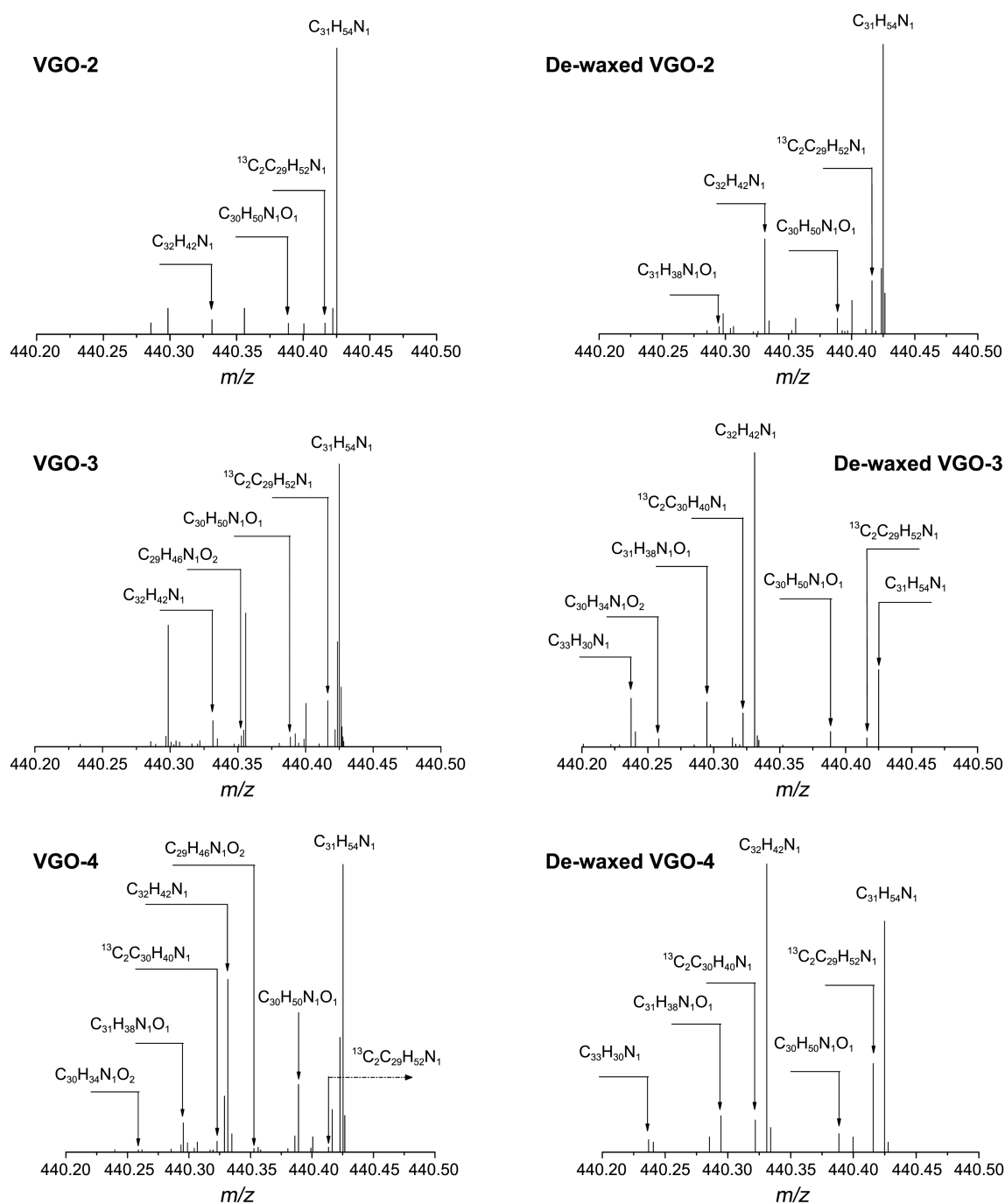
Figure 2. Mass scale expansion at a nominal mass of 440 Da for VGO cuts and their dewaxed oils.

waxed VGOs. Figure 1 shows the positive-ion ESI FT-ICR MS spectra of the VGO both before and after refining by solvent extraction. The molecular weight of the identified compounds ranged from 150 to 800 Da. The ESI FT-ICR mass spectra show that the molecular weight of identified compounds increased with increasing boiling point of the VGO fraction. The difference of the positive-ion ESI FT-ICR mass spectra between VGO and de-waxed VGO was the average molecular weight, of which those of the basic nitrogen species were higher in de-waxed VGO than those of the nitrogen species in its VGO. In a partial enlarged drawing (Figure 2), several kinds of nitrogen compounds are

all detected before and after refining when the m/z is between 440.20-440.50. So, it is very effective to use ESI FT-ICR MS to identify heteroatomic compounds in petroleum and its subfractions.

　Figure 3 shows the relative abundance of the positive-ion heteroatom class species in the VGOs and dewaxed VGOs. Among the basic nitrogen compounds N_1, N_2, N_1O_1, and N_1O_2 identified by the positive-ion mass spectra from VGOs, the N_1 class species were the most abundant, and N_1O_1 class species took the second place, which is similar to the results reported by other authors.[4,5,14] While N_1O_2 class was not found from VGO cut-2, and N_2 class was only
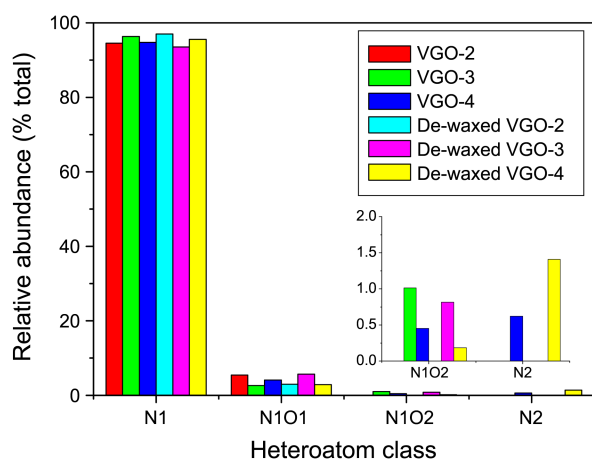
Figure 3. Heteroatom class distribution for VGOs and their de-waxed oils, based on positive-ion electrospray FT-ICR mass spectra.

identified from VGO cut-4, indicating the complexity of the basic nitrogen compounds increased with the increasing of boiling point of subfractions. In dewaxed VGOs, the N_1 class was also the predominant one, and followed by N_1O_1 class. Nitrogen atoms in nitrogen compounds tend to exist in ring structures, and there is almost no aliphatic nitrogen compound in petroleum.[4] The type and relative abundance of these basic nitrogen compounds in VGO were basically similar with the dewaxed VGO.

Mass Distribution and DBE *versus* Carbon Number Distributions for N_1 Class Species. Figure 4 shows the broadband positive-ion ESI FT-ICR mass spectra of the

identified N_1 class species from VGOs and dewaxed VGOs. The most abundant peaks of N_1 class compound for VGO cut-2 to cut-4 were at *m/z* 348, 382, and 404, respectively, and in dewaxed VGOs were at *m/z* 436, 490, and 490, respectively. The average molecular weight of N_1 compounds increased with increasing boiling point of the VGO fraction, and the molecular weight of N_1 compounds in dewaxed VGO shifted to the high value compared to VGO, suggesting that the relatively lower molecular weight N_1 compounds were easily removed during the base oil refining processes. The other basic nitrogen compounds identified from VGOs and dewaxed VGOs were also agreed with these findings.

The iso-abundance plot of DBE *versus* carbon number presenting the hydrogen deficiency of a given species, which provides detailed compositional data of the species, and is commonly used to analyze high-resolution mass spectra of crude oils.[2,15] Figure 5 shows the plots of DBE *versus* carbon number for the N_1 class species from the positive-ion ESI FT-ICR mass spectra of the VGOs and dewaxed VGOs. Generally, the basic N_1 compounds in the oil samples are mainly monoaromatic compounds, their DBE value is distributed between 4 and 21, including all kinds of N_1 compounds with different saturation. The basic N_1 compounds in the samples with a DBE value between 6 and 13 accounts for more than 80% of all N_1 compounds. The abundant basic N_1 class species in VGO cut-2, cut-3 and cut-4 had a DBE of 6-11, 6-9 and 7-13, respectively, and their carbon number spread over C_{23}-C_{30}, C_{25}-C_{32} and C_{26}-C_{34}, respectively. While in their dewaxed samples, DBE values of N_1 compounds with higher relative abundance is continuously distributed in
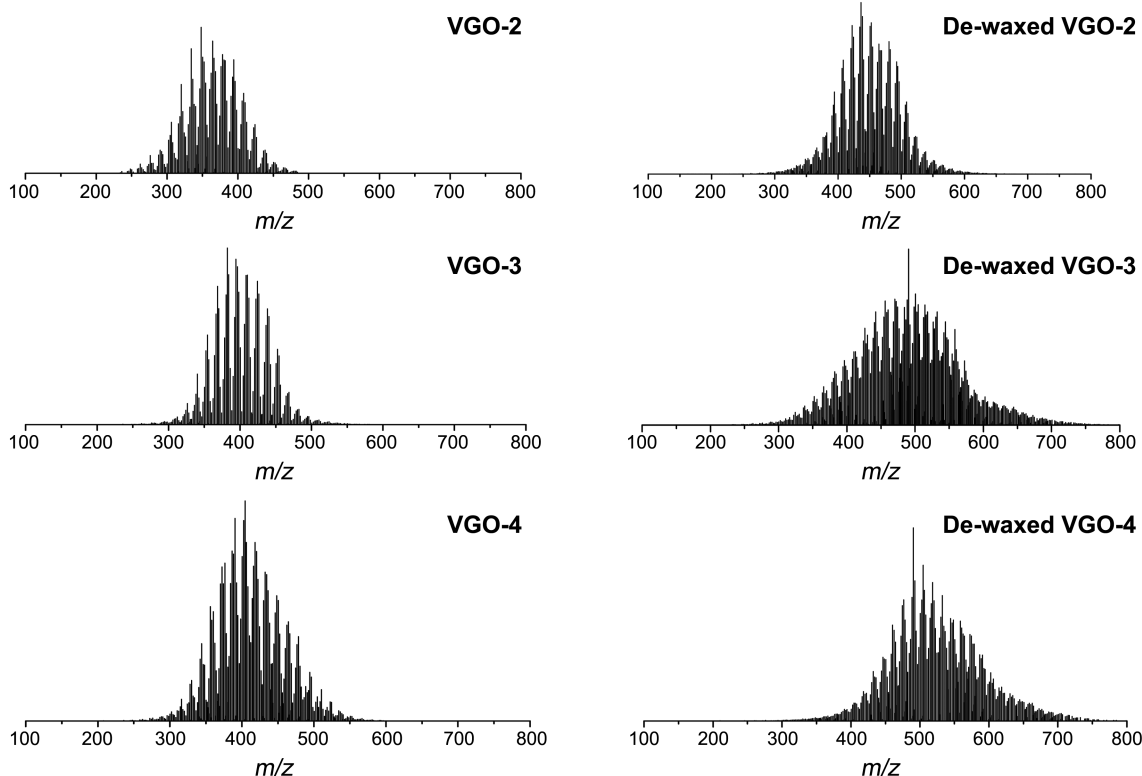
Figure 4. Broadband positive-ion ESI FT-ICR mass spectra of identified the N_1 class species in VGO cuts and dewaxed oils.
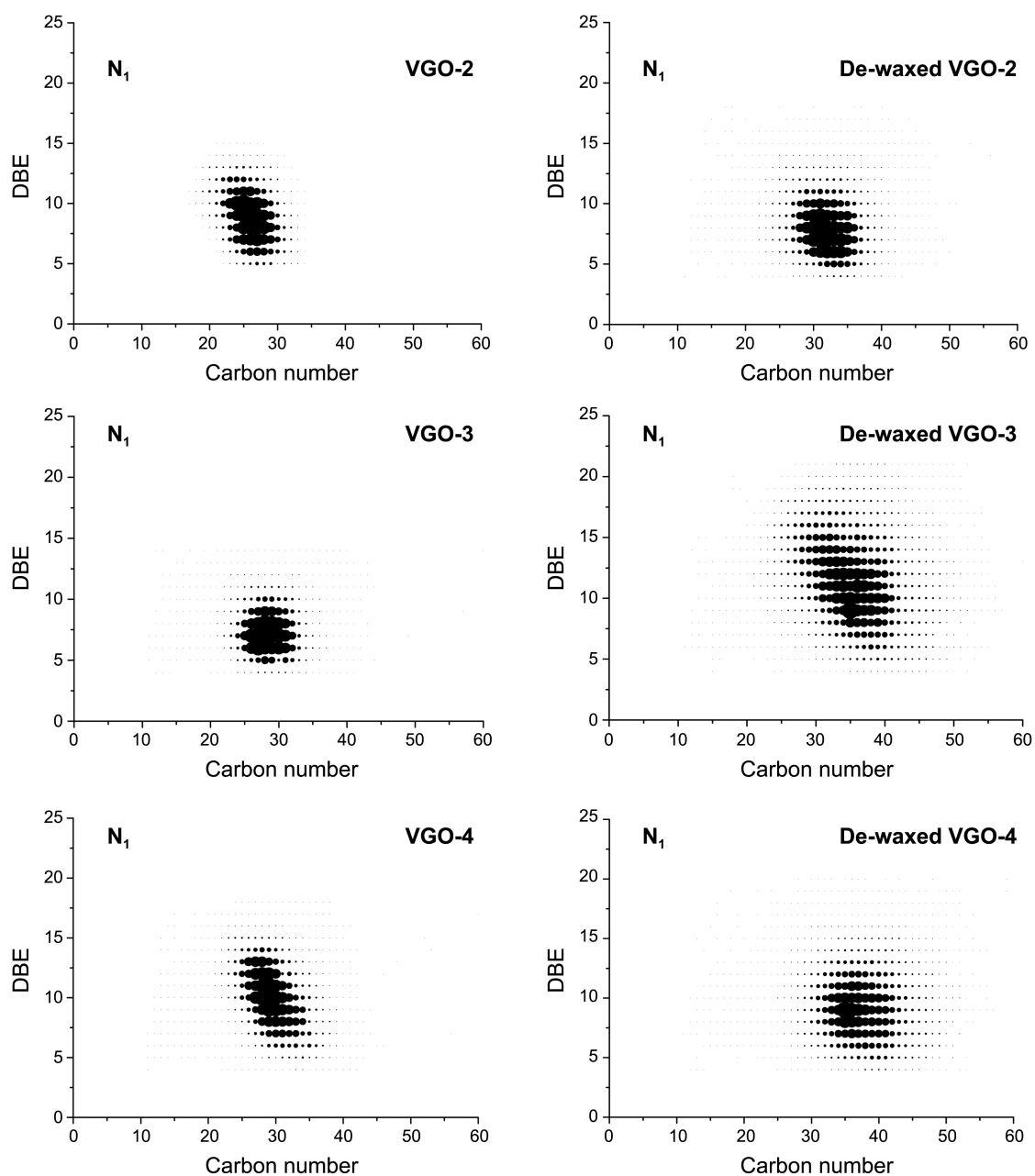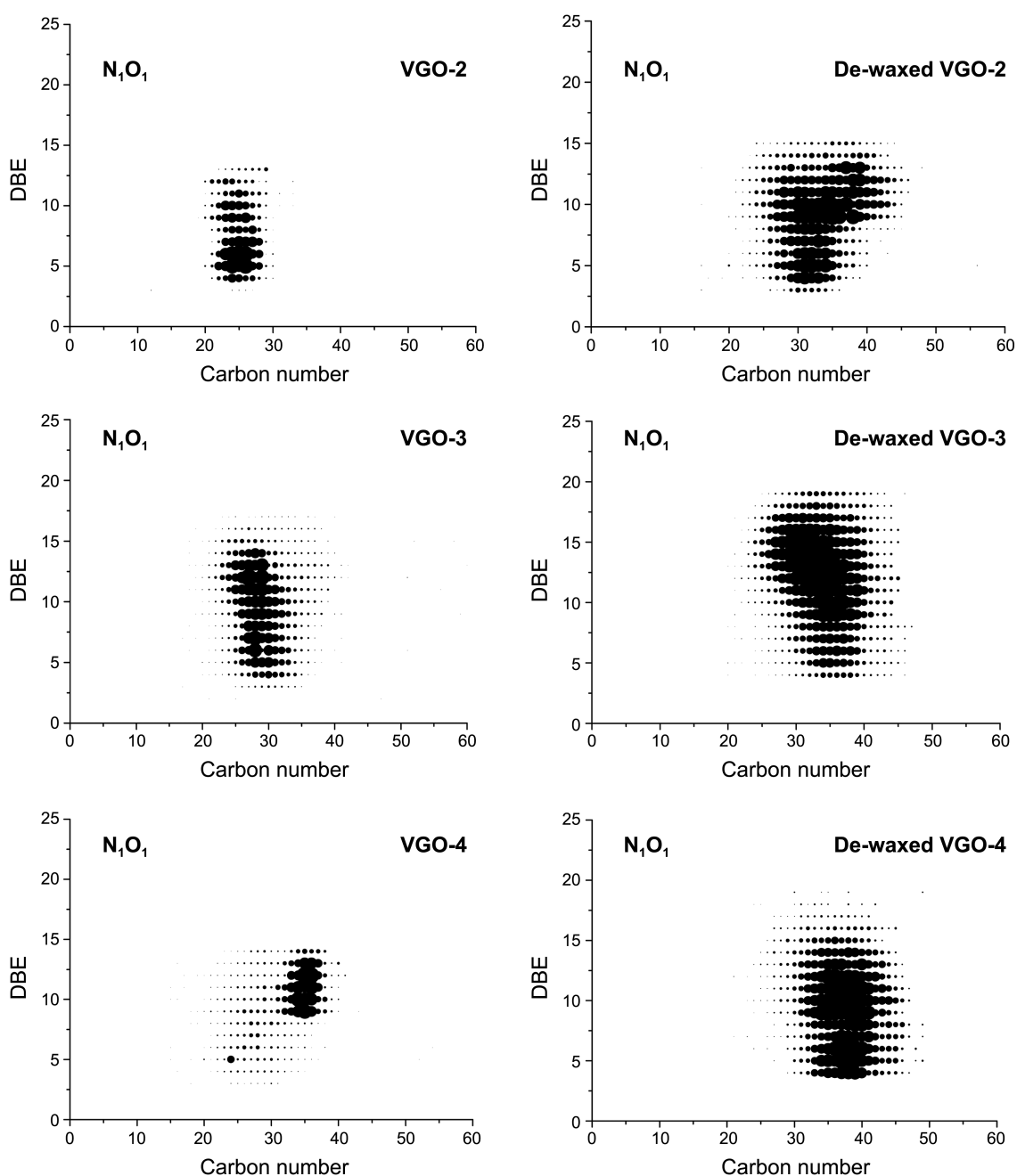
Figure 5. Plots of DBE as a function of the carbon number for N_1 class species from positive-ion ESI FT-ICR mass spectra of VGO cuts and their dewaxed oils.

6-10, 8-14 and 6-12, respectively, and their carbon number is centered at C_{28}-C_{36}, C_{31}-C_{40} and C_{33}-C_{42}, respectively. The main basic N_1 compounds in oil and its fractions are pyridine derivatives, quinoline derivatives, acridine derivatives.[4] From the above comparison to VGO and dewaxed VGO, it could be concluded that a certain amount of basic N_1 compounds with relatively smaller molecular weight and lower carbon number were significantly removed during the base oil refining process.

DBE *versus* Carbon Number Distributions for N_1O_1, N_1O_2 and N_2 Class Species. The relations between DBE and the carbon number in N_1O_1 compounds of the oil samples are showed in Figures 6, 7, and 8, respectively. The abundant N_1O_1, N_1O_2 and N_2 class species shifted to higher DBE

values and carbon numbers as the boiling point of the distillate fraction increased. Meanwhile, an obvious shift to higher carbon numbers for the N_1O_1 class species in dewaxed VGOs compared to VGOs was observed, this was the result of the refining process to VGO, N_1O_2 and N_2 class species also followed the similar trend. It was also observed that the DBE value and carbon number of dewaxed VGO seemed to be distributed a wider range compared to the VGO sample. This could be attributed to the difference of ionization efficiency for the nitrogen compounds in the different environment of VGO and dewaxed VGO, since the complexity of ionization efficiency is usually very difficult to be eliminated. Wu *et al.*[16] pointed out that the quantitative determination to all species identified is not currently
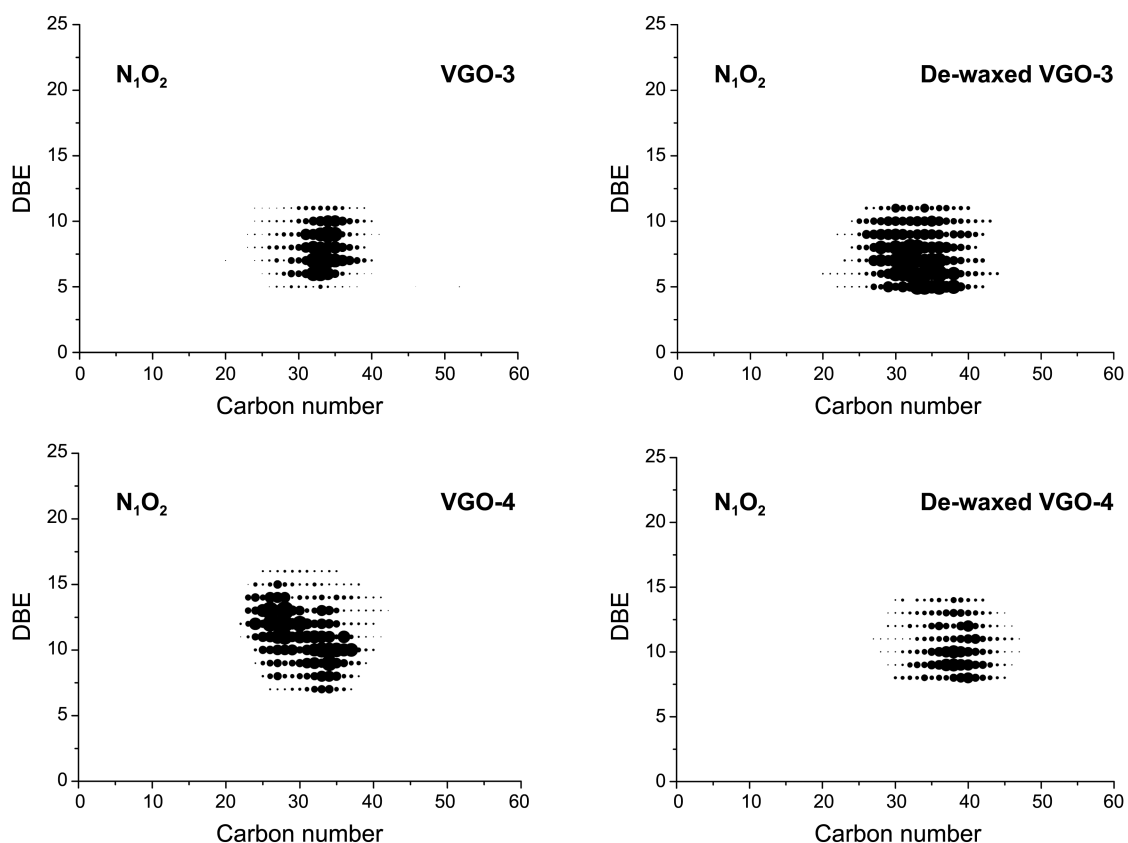
Figure 6. Plots of DBE as a function of the carbon number for N_1O_1 class species from positive-ion ESI FT-ICR mass spectra of VGO cuts and their dewaxed oils.

possible owing to the variation in ionization efficiency. The DBE value of N_1O_1 compounds lies between 4 and 19, suggesting that the molecular structures of individual N_1O_1 class species were significantly different. And the gap between the abundance of N_1O_1 compounds in dewaxed VGO with different DBE values is relatively very small, presenting an average distribution roughly. Even though the negative influence of variation of ionization efficiency existed in the experiment, it still could be concluded that N_1O_1, N_1O_2 and N_2 compounds with the lower carbon number tend to be removed selectively during the refining process.

The N_1O_1 class species are likely be comprised of a pyri-

dine ring and a furan ring or a double bond of carbon and oxygen.[5] While N_1O_2 class species may be suggested more complex structures: a pyridine ring and two furan rings, or a pyridine ring, a furan ring and a double bond of carbon and oxygen, etc. And the N_2 class species are likely amphoteric molecules including two heterocyclic rings: a pyridine ring and a pyrrole ring,[5] were enriched in the heavy fraction.

Generally, N_1 compounds are the most complex and predominant basic nitrogen compound, and there are almost no nitrogen compounds with a small number of carbons and low saturation. Although N_1O_1, N_1O_2 and N_2 class presented much lower relative abundance, they occurred over a wide

Figure 7. Plots of DBE as a function of the carbon number for N_1O_2 class species from positive-ion ESI FT-ICR mass spectra of VGO cuts and their dewaxed oils.
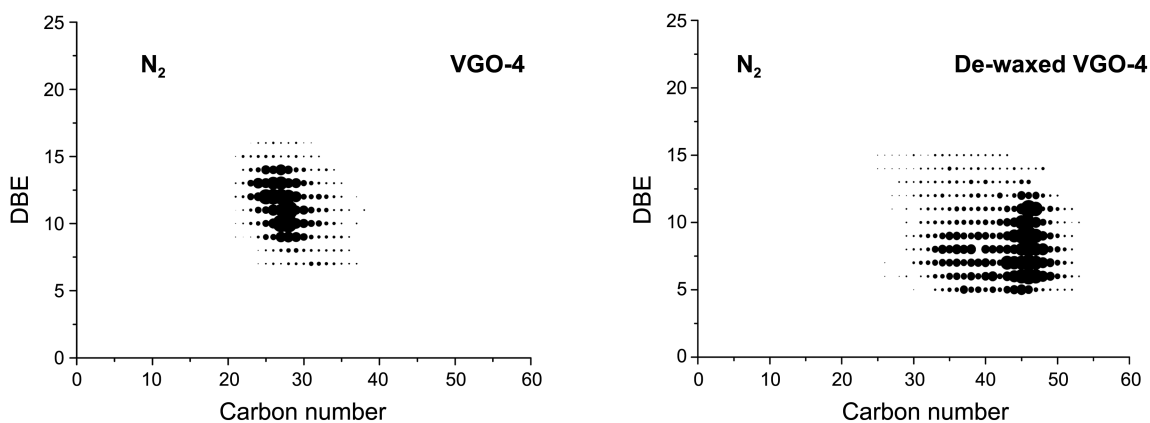
Figure 8. Plots of DBE as a function of the carbon number for N_2 class species from positive-ion ESI FT-ICR mass spectra of VGO cuts and their dewaxed oils.

range of DBE values, indicating a various degrees of condensed aromaticity. In lube base oil refining process of VGOs becoming dewaxed VGOs, the relatively smaller molecular weight and lower carbon number basic nitrogen compounds are more susceptible to be eliminated than those large molecular ones.

Conclusions

Detailed molecular compositions of basic nitrogen compounds in three VGO samples with different boiling point and their corresponding dewaxed VGOs were characterized by positive ESI FT-ICR MS. The analysis showed that basic nitrogen compounds were characterized by N_1, N_1O_1, N_1O_2, and N_2 class species, in which N_1 class species are the most abundant one accounting for more than 90% of the total abundance of all nitrogen-containing compounds, and followed by N_1O_1. Among them, N_1 class species in VGO cut-2, cut-3 and cut-4 were centered at C_{23}-C_{30} (*m/z* 300-430), C_{25}-C_{32} (*m/z* 350-460), and C_{26}-C_{34} (*m/z* 360-480), respectively, while in their corresponding de-waxed VGOs, the main N_1 compounds were at C_{28}-C_{36} (*m/z* 390-510), C_{31}-

C_{40} (*m/z* 420-560), and C_{33}-C_{42} (*m/z* 440-590), respectively. This indicated that with the increasing of boiling range, the carbon number and the average molecular weight of N_1 class species shifted to high values. In addition, the carbon number and average molecular weight of N_1 class species in de-waxed VGO were bigger than that of its parent VGO, which demonstrated that in the refining process of VGO to lube base oil by solvent extraction, more N_1 class species with relatively lower carbon number and lower average molecular weight were removed selectively. And N_1O_1, N_1O_2, and N_2 class species were also found to be in accordance with those findings.

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