Identification of acidic species extracted from heavy crude oil by fourier transform ion cyclotron resonance mass spectrometry

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Abstract−Acidic species were extracted from heavy crude oil by alcohol-alkali solution and ion exchange resin. The acidic species in the obtained extracts and extracted crude oil were characterized by negative-ion ESI FT-ICR MS. The analytical results indicated that some class species, O_2, O_1, N_1, N_1O_1, N_1O_2, N_1S_1 and O_2S_1 etc., were identified in the negative-ion spectrum, in which O_2, O_1 and N_1 class showed much higher abundance than others. Compared to O_1 and N_1 class, O_2 class could be extracted from heavy crude oil by using the two methods more efficiently, which means that a great majority of O_2 class can be extracted; meanwhile, almost half of O_1 and N_1 class still remained in residual phase. Detailed analysis demonstrated that alcohol-alkali method was effective for extracting O_2, O_1 and N_1 class with lower molecular weight; ion exchange method, however, was helpful to extract higher molecular weight O_1 and N_1 class and showed almost equal extraction selectivity to all kind of O_2 class.

Keywords: Acidic Species, Extraction, Heavy Crude Oil, ESI FT-ICR MS

INTRODUCTION

The exploration and utilization of heavy and inferior crude oil is more and more emphasized by many countries today since the conventional oil reserves are declining year by year due to the unavoidable fossil fuel scarcity. Heavier and more inferior crude oils may be a nice alternative for some refineries due to the relatively lower price of so-called "opportunity crude oils" [1-3]. One of the most important characteristics of heavy and inferior crude oils is their higher total acid number (TAN) besides higher density, viscosity and sulfur content etc. compared with conventional crude oil [2,4]. As one important marker, the TAN value was used to gauge the acidity of oils, defined as the mass of potassium hydroxide (in milligrams) required to neutralize acidic components in one gram of crude oil [2]. A higher TAN value means that there exist more acidic substances which are responsible for liquid phase corrosion in crude oil transport through pipelines and in refinery processing, and higher TAN value of oil products [1-7]. The corrosion caused by petroleum acids during the refining process is a major problem which should not be overlooked, so that now many researches for alleviating corrosion are mainly concentrated on removing petroleum acids from petroleum before refining. Extraction as one of the most important physical separation methods has been developed for years and yielded excellent fruits [8,9]. In the present work, the petroleum acids were extracted from crude oil by alcohol-alkali solution and ion exchange resin, respectively. In terms of the extraction method by alcohol-alkali solution, the process is introduced briefly as follows [10]. Naphthenates in crude oil could be transformed into the corresponding naphthenic acids and acetates under the solution of acetic acid-water. And acetates could dissolve in water phase and be removed by water-oil separation, while naphthenic acids could be extracted into water phase by using alcohol-alkali solution. Furthermore, after de-oil, acidification and solvent evaporation processes, naphthenic acids could be obtained [10]. And some references demonstrated that ion exchange resin could extract naphthenic acids from crude oil efficiently and exhibit a high selectivity [11]. Borgund et al. [12] found that extraction by using ion exchange resin exhibited a better performance compared to liquid-liquid extraction. Here, we have arbitrarily named alcohol-alkali method and ion exchange resin method as L-L method and S-L method, respectively.

In recent years, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has been successfully employed to analyze polar compounds in petroleum and its fractions because of its high resolving power, which means that it could resolve thousands of species in a single mass spectrum allowing for unambiguous determination of elemental composition [6,13, 14]. Positive-ion ESI could selectively ionize heteroatom species, such as basic nitrogen compounds [1,15-20], while negative-ion ESI could be used for the ionization of carboxylic acids (e.g., naphthenic acids, fatty acids), phenols and "neutral nitrogen" species (e.g., pyrrole homologues) [1,15,17-19,21-24] without derivatization or preconcentration of the sample, and with minimal sample consumption. Therefore, negative-ion electrospray could provides access to the most problematic components of petroleum such as acidic compounds we were concerned with from molecular level characterization for such a complex mixtures previously characterized only from their bulk properties [6].

We used alcohol-alkali solution and ion exchange resin to extract acidic species from heavy crude oil, and analyzed the residual crude oil of being extracted and the obtained acidic extracts by negative-

ion ESI FT-ICRMS. Based on the analytical results provided by ESI FT-ICR MS, some essential detailed information about the compositional changes of acidic species in heavy crude oil during the extraction process could be learned, which may help us to understand and evaluate the two different extraction methods, and thus determine their difference. This work will provide a clearer understanding of the separation of petroleum acids from crude oil by extraction.

EXPERIMENTAL SECTION

1. Samples

The heavy crude oil sample was supplied by the Liaohe Petrochemical Branch Company, PetroChina. And some basic properties of this crude oil were measured according to the related standards. The density at 20 °C is 0.9781 g/cm³, the viscosity at 20 °C is 60.606 Pa·s, the water content and total acidic number (TAN) are 1.40 wt% and 3.61 mgKOH/g, respectively. From above basic properties, Liaohe heavy crude oil has a much higher density, viscosity, and TAN value, implying it is a highly acidic extra-heavy crude oil.

Fig. 1 shows the TAN value of each narrow fraction of heavy crude oil. distillates with boiling range of 160-260 °C had a low TAN value of less than 0.5 mgKOH·g⁻¹, the TAN value of distillates increased dramatically from 0.10 to 9.08 mgKOH·g⁻¹ within the boiling range of 200-400 °C, and then sharply fell to 5.50 mgKOH·g⁻¹ in the range of 400-420 °C. Moreover, there were no obvious gaps between each distillate within 400-480 °C, and eventually, the TAN value leaped to 8.42 mgKOH·g⁻¹ within 480-496 °C, which was still lower than that within 380-400 °C (9.08 mgKOH·g⁻¹).

Acidic species can be separated from crude oil and distillates by many methods. In this work, acidic species were extracted from heavy crude oil by alcohol-alkali solution and ion exchange resin, respectively; the detailed procures are described in references [10, 11]. The samples were analyzed by ESI FT-ICR MS including acidic extracts and their residual crude oils.

2. Sample Preparation for ESI FT-ICR MS Analysis

The sample preparation method for the analysis of acidic species in acidic extracts and residues samples by negative-ion electrospray FT-ICR MS has been previously reported [1,6,21,22,24, 25-27]. For each sample, 10 mg was completely dissolved in 1 mL toluene. And then, for each mixture solution, it was diluted to 0.2 mg/mL with a mixture solvent of toluene/methanol (1 : 1 v/v). For each diluted solution, it was then added with 15 μL of 28% NH₄OH to facilitate the deprotonation of acidic species to yield [M-H]⁻ ions [6,28]. The toluene and methanol were both analytical-reagent-grade, and were distilled several times and kept within glass bottles with ground glass stoppers.

3. ESI FT-ICR MS Analysis

Samples were analyzed with a Bruker apex-ultra FT-ICR MS equipped with an actively shielded 9.4 T superconducting magnet. The sample was infused by an Apollo II electrospray source at a flow rate of 180 μL/h using a syringe pump. The operating conditions for negative-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. The delay was set to 1.2 ms to transfer ions to an ICR cell by the electrostatic focusing of transfer optics. The data size was set to 4 M words, and time-domain data sets were co-added from 128 data acquisitions.

4. Mass Calibration and Data Analysis

The mass spectra obtained were calibrated internally according to the most abundant homologous series compounds. All masses were then converted to the Kendrick mass scale [6]. The Kendrick-sorted masses with relative abundance greater than six times the standard deviation of the baseline noise were imported into an Excel spreadsheet for identification. Data analysis was implemented by using custom software which had been described by some references [1,6,14,24]. Generally, a two-mass scale-expanded segment in the middle of the mass spectrum was selected for calibration during data analysis, and then detailed identification of each peak would be carried out [6,25]. Compounds of a homologous series would be identified according to Kendrick mass defect (KMD), and the essence was that compounds with the same heteroatom composition and number of rings plus double bonds (DBE), but different numbers of CH_2 groups, have identical Kendrick mass defect (KMD) [6,10,24,29].

RESULTS AND DISCUSSION

1. Mass Distribution

Broadband negative-ion electrospray 9.4 T FT-ICR MS identified thousands of acidic species in all samples, as shown in Fig. 2.

From Fig. 2, acidic species in extracts from heavy crude oil by L-L method were distributed over 250-650 Da and acidic species in residues was 250-900 Da. And for S-L method, the acidic species in extracts and residues were distributed in 250-820 Da and 200-800 Da, respectively. All mass spectra exhibited normal distributions. The broadband ESI mass spectra of these samples indicated that the ionization efficiency was not limited by molecular weight or compositional complexity [6].

Choose some mass point with better signal-to-noise ratio (SNR), and it can be seen that there are multiple mass peaks in the range of one unit mass point when the mass spectra was unfolded further, as an example of mass point 366 Da of mass spectra of acidic extracts by L-L method. The importance of ultrahigh mass resolving power and mass accuracy in the determination of acidic species in
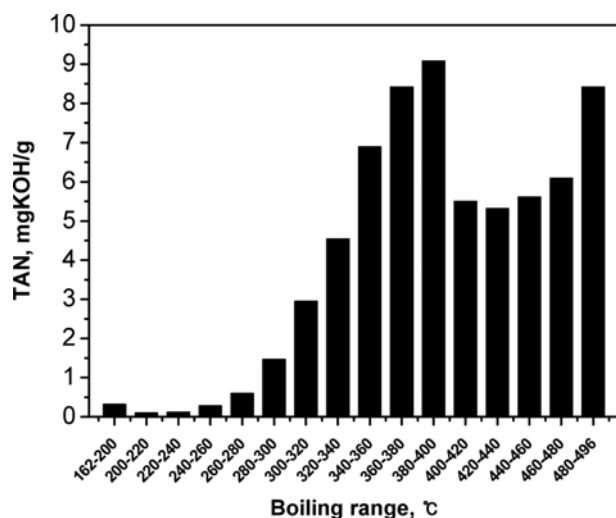

Fig. 1. The TAN of narrow fractions in Liaohe crude oil.

Acidic extracts by L-L method

Extracted crude oil by L-L method

Acidic extracts by S-L method

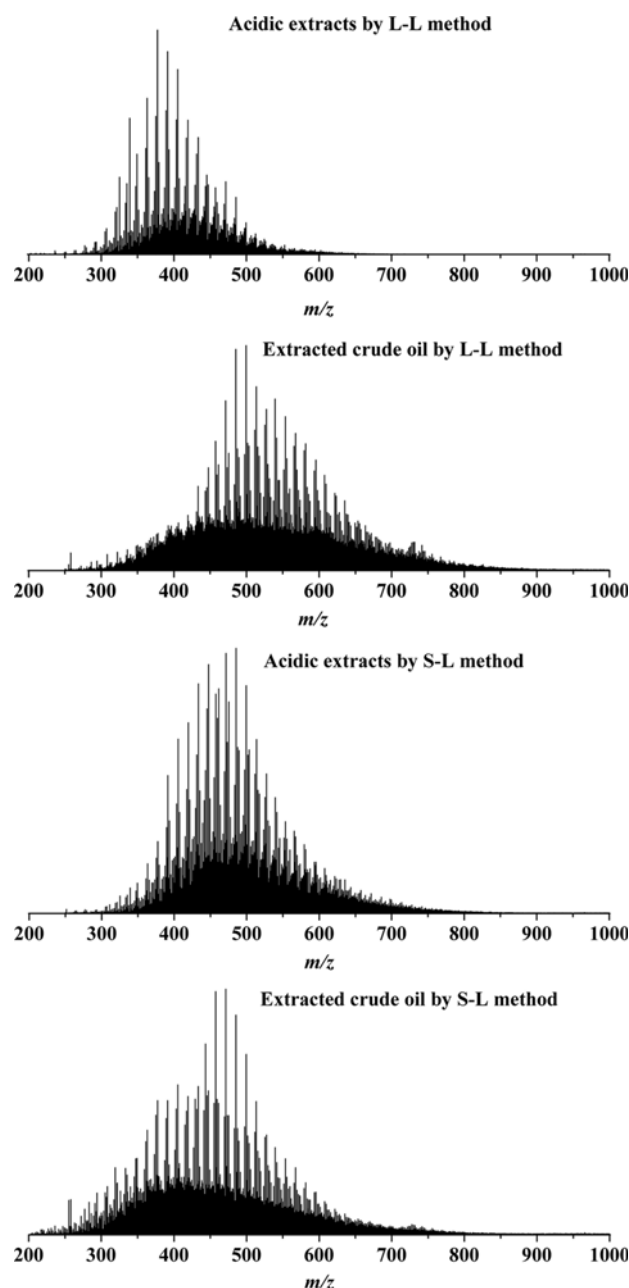## Extracted crude oil by S-L method

Fig. 2. Broadband negative-ion ESI FT-ICR mass spectra of extracts and the residues.

the samples is evident from Fig. 3. The mass errors between the observed and theoretical masses at 366 Da are in Table 1.
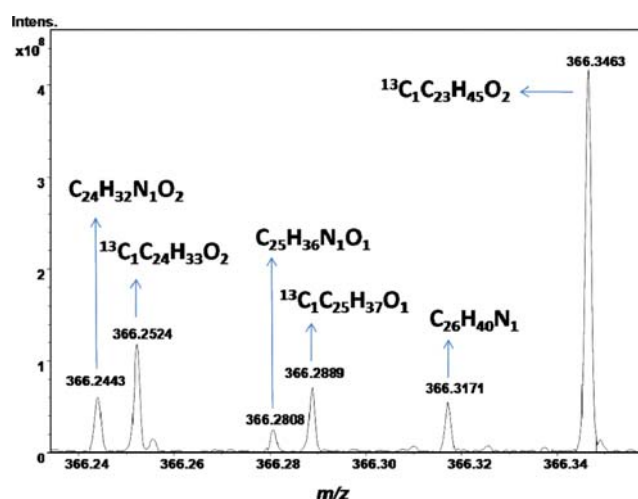

Fig. 3. Mass scale expansion at a nominal mass of 366 Da for acidic extracts by L-L method.

2. Heteroatom class composition

Even if the absolute abundance of a given class is the same for two samples, the relative abundance will depend on differences in absolute abundances of the other species [6]. Therefore, the absolute abundance would be adopted in Fig. 4, and this would also facilitate making a comparison of the abundance for a given class species in each oil sample directly.

Fig. 4 shows the abundance represented by intensity of mass peak of acidic compounds comprising heteroatom class identified by negative-ion electrospray FT-ICR MS in each sample; and acidic compounds N_1, O_1 and O_2 class species were identified and accounted for more than 80% of the total mass peak abundance, and another identified class such as N_1O_1, N_1O_2, N_1S_1, O_2S_1 etc. were not listed here. The abundance of O_2 class species extracted by the two methods was much higher than O_2 class species in their extracted heavy crude oil, respectively, but for O_1 and N_1 class species, their abundance in acidic extracts was slightly lower than that in their residual phase. Meanwhile, for the two methods, the abundance of O_2, O_1 and N_1 class species showed not too much difference in extracted crude oil; however, in the acidic extracts, the abundance of O_2 class species was much higher than O_1 and N_1 class species. This indicated that O_2 class species can be capable of being extracted from heavy crude oil by using the above methods more efficiently compared to O_1 and N_1 class species.

The identified O_2 class species were presumably carboxylic acids (fatty and naphthenic acid), which are mainly responsible for high TAN value of heavy crude oil. N_1 class species were neutral nitro-

Table 1. Mass errors between the observed and theoretical masses (366 Da) for acidic extracts by L-L method

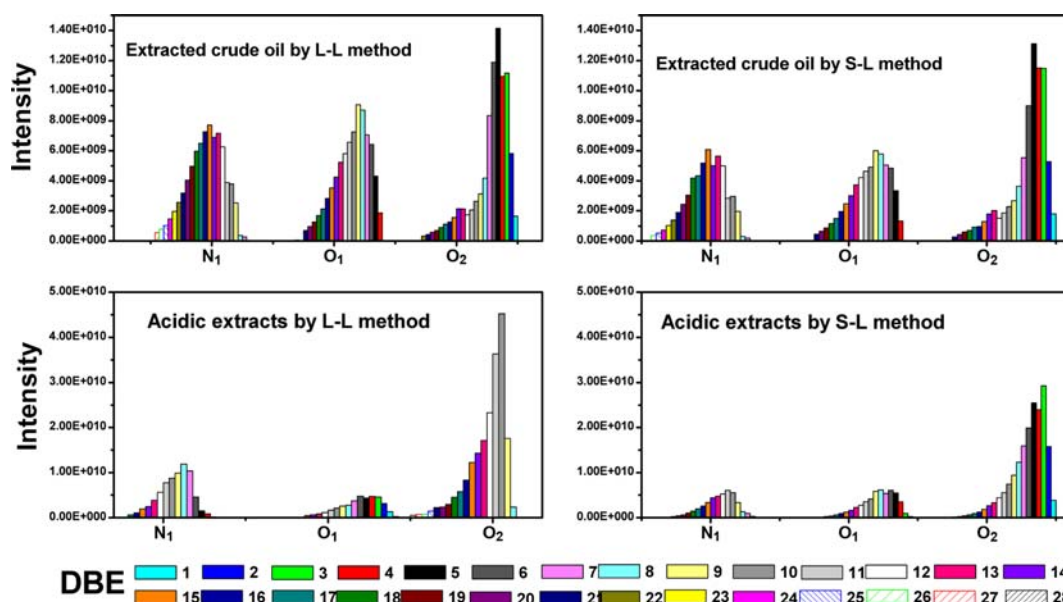| #	Mol.Formula	Measured m/z	m/z	err [mDa]	|err| [ppm]	err [ppm]	Mean err [ppm]	Sigma
1	$C_{24}H_{32}N_1O_2$	366.2443	366.2439	−0.43	1.2	−1.2	0.1	0.1034
2	$^{13}C_1C_{24}H_{33}O_2$	366.2524	365.2486	−0.42	1.1	−1.1	−1.6	0.0286
3	$C_{25}H_{36}N_1O_1$	366.2808	366.2802	−0.55	1.5	−1.5	−6.4	0.1700
4	$^{13}C_1C_{25}H_{37}O_1$	366.2889	365.285	−0.48	1.3	−1.3	−1.6	0.0086
5	$C_{26}H_{40}N_1$	366.3171	366.3166	−0.52	1.4	−1.4	−5.3	0.1156
6	$^{13}C_1C_{23}H_{45}O_2$	366.3463	365.3425	−0.38	1.1	−1.1	−1.5	0.0548

Fig. 4. Class species distribution for extracted crude oil and acidic extracts based on negative-ion ESI FT-ICR MS (Only classes N_1, O_2 and O_1 are shown).
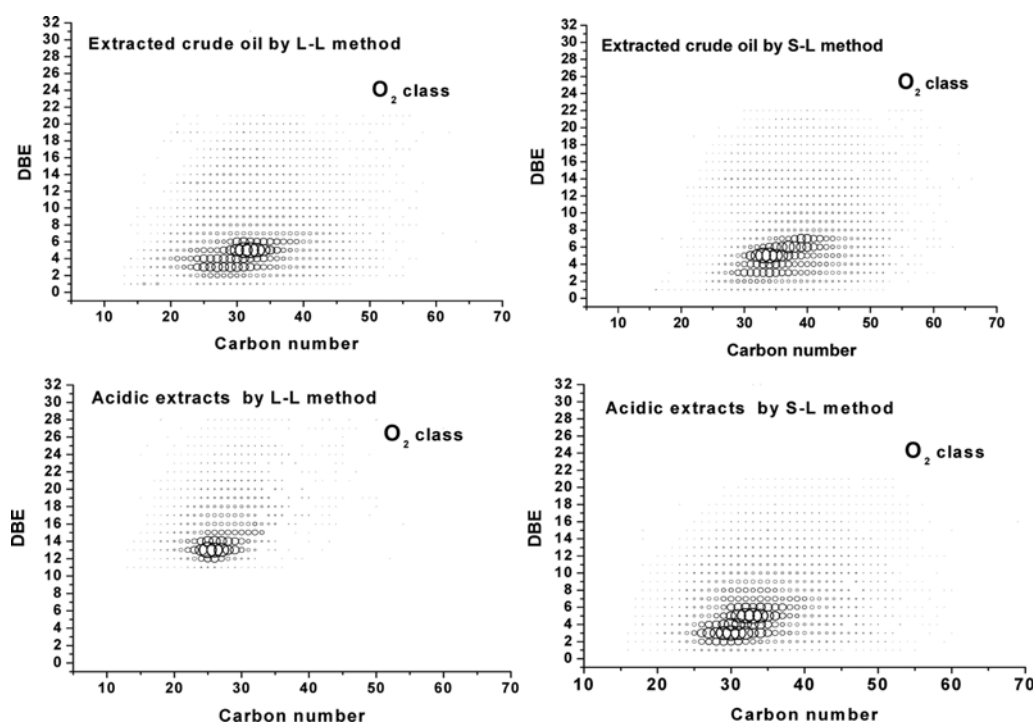

Fig. 5. Plots of DBE as a function of the carbon number for O_2 class species from negative-ion ESI FT-ICR mass spectra of extracted crude oil and acidic extracts.

gen compounds such as carbazoles, since basic nitrogen compounds could not be ionized by negative-ion ESI. It was very likely that O_1 class species belong to compounds with phenolic hydroxyl [2,22,25].

3. DBE Versus Carbon Number Distributions for O_2 Class Species

Fig. 5 shows the plots of DBE versus carbon number for O_2 class species from the negative-ion ESI FT-ICR mass spectra. The acidic extracts obtained by L-L method had a DBE of 11-28 and carbon number of C_{13}-C_{60}, and the most abundant O_2 class species had a DBE

of 13, which were most likely aromatic carboxylic acids. Meanwhile, the DBE of O_2 class species in residual phase was 1-22 and their carbon number distributed C_{16}-C_{66}. Therefore, it could be concluded that the L-L method was mainly capable of extracting O_2 class species with smaller molecular weight but bigger DBE value selectively, that is, the smaller molecular aromatic carboxylic acids were relatively easier to be removed from crude oil by using L-L extraction method.

And for S-L extraction method, the acidic extracts distributed DBE

and carbon number over 1-32 and C_{16}-C_{69}, respectively, in which the most abundant O_2 class species with DBE of 5 were usually regarded as naphthenic acids with four naphthenic rings. While in its extracted

crude oil, DBE of O_2 class species was at 1-31, carbon number was at C_{13}-C_{66}. This comparison revealed that S-L method was effective in the removal of O_2 class species in heavy crude oil and presented
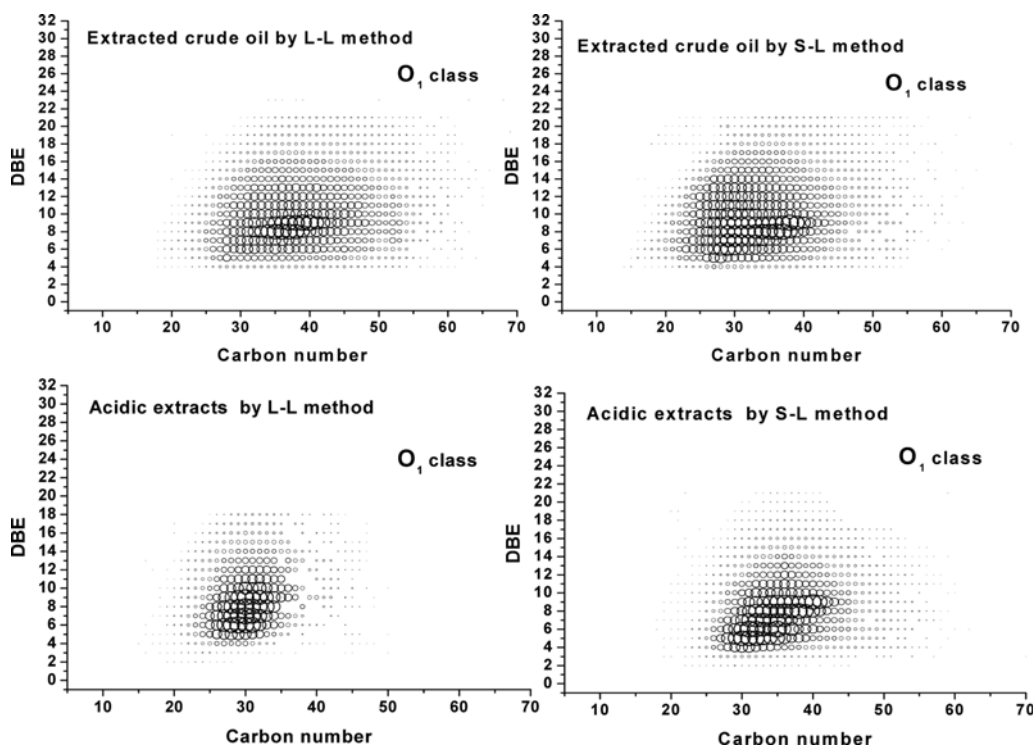

Fig. 6. Plots of DBE as a function of the carbon number for O_1 class species from negative-ion ESI FT-ICR mass spectra of extracted crude oil and acidic extracts.
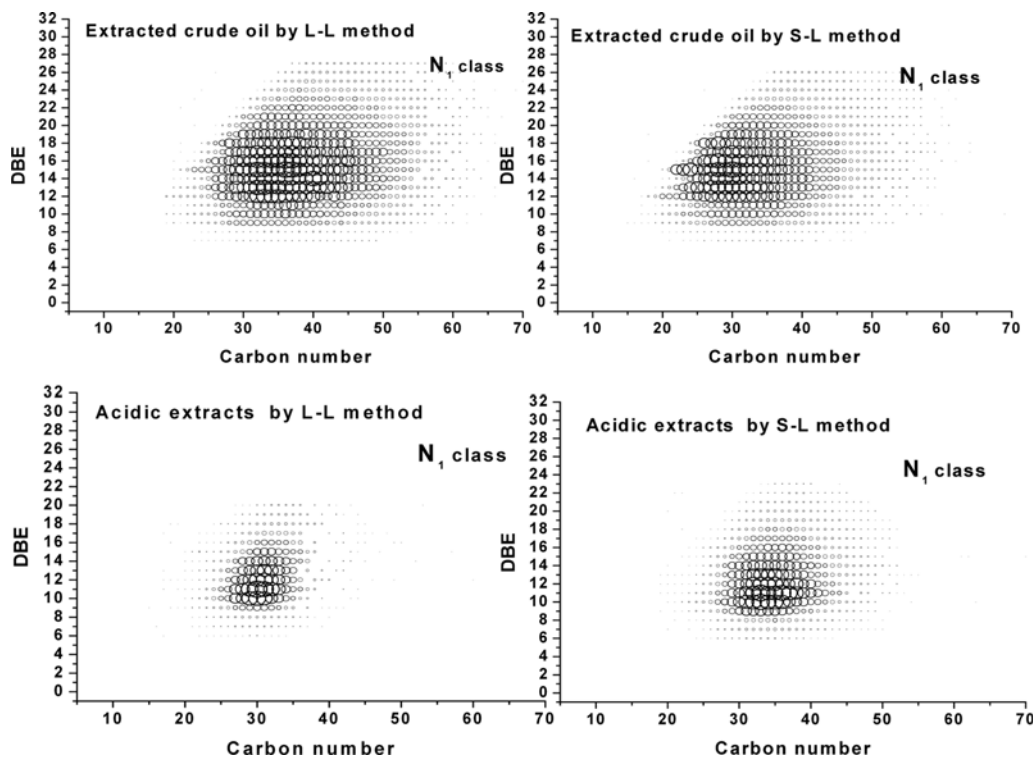

Fig. 7. Plots of DBE as a function of the carbon number for N_1 class species from negative-ion ESI FT-ICR mass spectra of extracted crude oil and acidic extracts.

almost equal selectivity for all kinds of naphthenic acids.

4. DBE Versus Carbon Number Distributions for O_1 Class Species

The charts of DBE as a function of the carbon number for the O_1 class species are shown in Fig. 6. These O_1 class species were considered as alkyl phenols or aromatic phenols [7,25]. The O_1 class species in acidic extracts obtained by L-L method mainly had DBE of 5-12 and carbon number of C_{25}-C_{35}, and those most abundant O_1 class species in extracted crude oil were centered at DBE of 5-14 and carbon number of C_{30}-C_{45}. In terms of the S-L method, DBE of O_1 class species in acidic extracts distributed in 4-12 and carbon number of C_{30}-C_{40}, and in its residual phase, that was DBE of 5-15 and carbon number of C_{25}-C_{40}. Therefore, L-L method mainly tended to extract O_1 class species with lower molecular weight, and left those higher molecular weight O_1 compounds remaining in extracted crude oil. However, the S-L method exhibited its preference for extracting O_1 class species with higher molecular weight, which was significantly different from the L-L method.

5. DBE Versus Carbon Number Distributions for N_1 Class Species

The charts of DBE as a function of the carbon number for the N_1 class species were presented in Fig. 7. From Fig. 7, it can be seen that the amount of N_1 class species in acidic extracts were much less than that in extracted crude oil, and the range of DBE value of N_1 class species in acidic extracts were narrower. By comparing each chart of Fig. 7, the L-L method plays an effective role to extract N_1 class species with lower molecular weight (DBE of 10-15 and carbon number of C_{25}-C_{35}) in heavy crude oil. Whereas, the S-L method was more suitable to extract higher molecular weight N_1 class species (DBE of 9-15 and carbon number of C_{30}-C_{40}).

CONCLUSION

The analytic results from negative-ion ESI FT-ICR MS demonstrated that O_2, O_1 and N_1 had much higher abundance than other identified class species such as N_1O_1, N_1O_2, N_1S_1, O_2S_1 etc. A great majority of O_2 class species can be extracted from heavy crude oil by using the two methods; meanwhile, O_1 and N_1 class species exhibited lower extraction efficiency since almost half of them still remained in residual crude oil. L-L method was mainly effective for the extraction of O_2, O_1 and N_1 class species which were lower molecular weight; however, the S-L method showed its preference to higher molecular weight O_1 and N_1 class species and showed almost equal selectivity of extraction to all kinds of O_2 class.

ACKNOWLEDGEMENT

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