Oil Shale, 2013, Vol. 30, No. 1, pp. 76–89
doi: 10.3176/oil.2013.1.07

ISSN 0208-189X

INFLUENCE OF HEATING RATE ON BASIC NITROGEN-CONTAINING SPECIES CONTENT IN DACHENGZI SHALE OIL STUDIED BY POSITIVE-ION ELECTROSPRAY IONIZATION FT-ICR MASS SPECTROMETRY

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Abstract. *Shale oil samples were produced by pyrolysis of Dachengzi oil shale, China, in a fixed bed reactor at a heating rate ranged from 5 to 20 °C min*$^{-1}$ *under argon atmosphere, at the same final temperature of 520 °C and residence time of 20 minutes. Positive-ion electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) was employed to study the influence of heating rate on the basic nitrogen species content in the shale oil. The results show that increasing the heating rate results in the increase of total and basic nitrogen contents and the number of basic nitrogen species. Among all basic classes identified from positive-ion ESI FT-ICR mass spectra, the relative abundance of* N_1 *class decreases while that of* N_1O_1, N_1O_2, N_1O_3 *and* N_2 *classes increases as heating rate increases. With increasing heating rate the relative abundance of pyridines, whose DBE is 4, decreases significantly and that of* N_1 *class species with DBE = 5–11 slightly, while species with DBE over 11 increase slightly. Furthermore, for pyridines and quinolines (DBE = 7) a relative obvious decrease in relative abundance is mainly observed in those species whose carbon numbers remain between 21 and 37 as heating rate increases. The relative abundance of* N_1O_1 *and* N_1O_2 *class species, whose DBE is in the range of 10–21, increases.*

Keywords: *pyrolysis, heating rate, nitrogen-containing species, positive-ion ESI FT-ICR MS.*

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1. Introduction

Shale oil is one of the most complex chemical mixtures, comprising thousands of hydrocarbons and nitrogen-, oxygen- and sulfur-containing compounds [1–8]. The nitrogen present in shale oil is usually divided into two broad types: basic nitrogen and neutral nitrogen. It is well known that the presence of nitrogen in shale oil can cause serious problems in oil processing and affect adversely the stability of its products [9–12]. Basic nitrogen compounds (e.g., pyridine homologues) in oil are particularly resistant to hydrotreatment [11] and are stronger inhibitors of hydrodesulphurization reactions than neutral nitrogen compounds in oil [12], reducing the efficiency of S and O removal [13, 14]. These compounds are also often involved in the formation of gums, lacquers and precipitates [15]. On the other hand, combustion of shale oil leads to emissions of NO_x because of the presence of nitrogen in shale oil [11, 15, 16]. Again, some polycyclic aromatic nitrogen hydrocarbons (PANH) present in the aromatic fraction of shale oil, such as quinolines and methylquinolines, are extremely harmful to human health due to their toxicity, mutagenicity and carcinogenicity [15, 16]. Considering these negative consequences, an insight into basic nitrogen compounds in shale oil is most important and highly necessary in order to optimize methods for their removal and to specify procedures for the safe handling of such materials.

Many studies have been conducted on basic nitrogen compounds in shale oil and its products [1–4, 9, 11, 15–18]. Based on the results of early studies of raw Green River shale oils Poulson [9] concluded that basic nitrogen compounds in shale oil are principally of pyridine type with small amounts of amines present. Subsequently, many researchers applied gas chromatographic (GC) and/or gas chromatographic-mass spectrometric (GC-MS) techniques to investigating basic nitrogen compounds in various shale oils [1–4, 15–18]. The results of GC-MS and/or GC analysis on basic nitrogen compounds in shale oils are similar to those summarized by Poulson and also indicate that the basic nitrogen species with a low molecular weight can be well characterized by these techniques. However, these methods are still incapable of identifying accurately nitrogen compounds with a high molecular weight (especially greater than 300 Da) due to their low volatility and low concentrations [19, 20]. In addition, because of the low mass resolving power and selectivity for nitrogen compounds in traditional MS, the oil sample needs to be prefractionated to either isolate nitrogen compounds from a predominately hydrocarbon matrix or concentrate them prior to analysis, which generates difficulties in designing the separation scheme [20, 21].

Recently, another powerful analytical technique, electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has been widely used for characterizing basic nitrogen-containing species in various liquid fuels, including crude oil and its products [20–25] and shale oil [26–28]. FT-ICR MS can afford ultrahigh mass resolution ($m/\Delta m_{50\%}$ > 300 000, in which $\Delta m_{50\%}$ denotes mass spectral peak full width at half height) and high mass accuracy (< 1 ppm), enabling the identification of thousands of polar species in a single mass spectrum [23, 24]. Moreover, in case of this analytical technique, the time-consuming separation scheme prior to analysis is not necessary to isolate and concentrate basic nitrogen compounds [20, 24] and therefore the analysis is more time-saving.

Although basic nitrogen-containing species in shale oil have been extensively characterized using various analytical techniques, including GC, GC-MS and FT-ICR MS, the latter method has not been applied to examining the effect of different pyrolysis conditions on the distribution of these species in shale oil yet. Hence, we employ positive-ion ESI FT-ICR MS to investigate the effect of heating rate on the basic nitrogen-containing species distribution in the shale oil produced by pyrolysis of Dachengzi oil shale, China, including their relative abundance, value of rings plus double bonds (double bond equivalents, DBE) and carbon number (C_n).

2. Experimental

2.1. Shale oil samples

The sample of oil shale, whose general characteristics have been reported in the literature [29], was obtained from the fourth seam of the Dachengzi deposit located in Huadian city, China. Every 50 g of dried oil shale sample (particle size < 3 mm) was pyrolyzed in the fixed bed reactor (Fig. 1) to the final temperature of 520 °C and held at that temperature for 20 minutes. The reactor was externally heated by an electric ring furnace and temperature

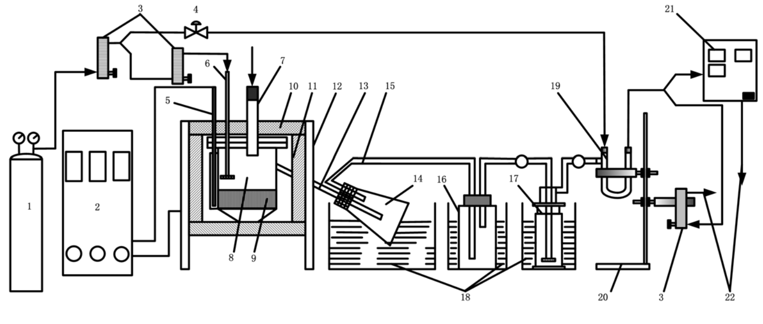

Fig. 1. Schematic diagram of the fixed bed reactor.

1 – argon cylinder, 2 – automatic temperature controller, 3 – flowmeter, 4 – flow control valve, 5 – thermocouple, 6 – gas inlet, 7 – sample inlet, 8 – retort reactor, 9 – oil shale, 10 – insulation, 11 – electric heater, 12 – steel stand, 13 – copper tube, 14 – conical flask, 15 – silicone tube, 16 – wide-mouthed bottle, 17 – gas washing bottle, 18 – water/ice condenser, 19 – U-tube, 20 – stand, 21 – gas analyzer, 22 – vent.

was controlled by a proportion integration differentiation (PID) controller. The heating rates were 5, 8.5, 12 and 20 °C min^{-1}. Argon as the carrier gas was purged at a fixed flow rate of 300 mL/min through the reactor for sweeping the evolved products quickly from the reaction zone, to reduce the extent of secondary reactions [30, 32]. The liquid oil phase was trapped in the conical flask inside a water/ice condenser (Fig. 1). The oils consisted of an aqueous phase and an oil phase. The procedure of separation of oil from the aqueous phase was the same as that described in the literature [8, 16]. Finally, the oil samples were stored in refrigerated conditions prior to analysis.

2.2. Positive-ion ESI FT-ICR MS analysis

Every 10 mg of oil sample was completely dissolved in 1mL of toluene. A total of 20 µL of the solution mixture was diluted with 1 mL of a toluene/ methanol (1:1, v/v) solution. Next, methanoic acid, at a volumetric ratio of 5 µL to every 1 mL of the sample solution, was added to ensure efficient protonation for positive-ion ESI analysis. The toluene and methanol used were analytical reagent grade solvents, which were distilled twice and kept in glass bottles with ground glass stoppers [21].

For each shale oil sample mass analysis was performed with a Bruker apex-ultra FT-ICR MS (Bruker, Germany) equipped with an actively shielded 9.4 T superconducting magnet. The sample solution was infused at a flow rate of 180 µL/h. Typical operating conditions for positive-ion ESI were: emitter voltage, –4.1 kV; capillary column front end voltage, –4.6 kV; and capillary column end voltage, 320V. The ions accumulated within 0.001 s in a hexapole with 2.4 V direct-current (DC) voltage and $700V_{p-p}$ radiofrequency (RF) amplitude. The optimized mass for quadrupole 1 (Q1) was 180 Da. An argon-filled hexapole collision pool was operated at 5 MHz and $500V_{p-p}$ RF amplitude, in which the ions accumulated within 0.001 s. The delay was set to 1.1 ms to transfer the ions to an ICR cell by electrostatic focusing of transfer optics. The ICR was operated at 11 db attenuation, 150–800 Da mass range, and 4 M acquired data size. The time domain data sets were co-added from 64 data acquisitions.

2.3. Mass calibration and data analysis

Mass spectrometry was performed using calibration by sodium formate before analysis. The internal calibration was used for the mass spectra of shale oil with a known and rather abundant homologous series of nitrogen-containing compounds. The peaks with a relative abundance greater than 5 times the standard deviation of the baseline noise were exported to an Excel spreadsheet. Data analysis was carried out using the software developed by Zhu *et al*. and its procedure has been described in the literature [21]. In brief, first, a two-mass scale-expanded segment in the middle of the spectrum was selected and then each peak was identified. The peak of at least one of each heteroatom class species was arbitrarily selected as the reference [21]. Both species of the same class and their isotopes with different values of DBE and carbon number were searched within a set of ±0.001 Kendrick mass defect (KMD) tolerance [31].

3. Results and discussion

3.1. Influence of heating rate on nitrogen content in shale oil

Table 1 presents the yield of oil and nitrogen content in the shale oil obtained by the pyrolysis of Dachengzi oil shale carried out at a heating rate varied from 5 to 20 ^{o}C min^{-1}. It can be seen from this table that the oil yield increased with the increase of heating rate from 5 to 20 ^{o}C min^{-1}. This finding agrees with that reported by Nazzal [30] and Williams and Ahmad [32]. Besides, the total and basic nitrogen contents in shale oil also increased with increasing heating rate. This indicates that higher heating rates contribute to increasing the oil yield but meanwhile lead to the transformation of more nitrogen present in oil shale into shale oil at a heating rate of 5–20 ^{o}C min^{-1}. The high nitrogen content in raw shale oil probably makes denitrogenation during the refinery process more difficult, resulting in the increase of the cost of nitrogen removal. Concerning the influence of heating rate on the oil yield during pyrolysis, Williams and Ahmad [32] consider that low oil yield at low heating rates may be attributed to the formation of a carbonaceous residue or coke via secondary reactions of the liquid oil. They also suggest that heating rate influences the formation of the autogeneous intraparticle gas which sweeps the oil vapours from the oil shale, higher heating rates generate higher intraparticle gas sweep rates and lead to less oil degradation. The fact that the shale oil produced from the pyrolysis of Dachengzi oil shale at a higher heating rate contains more nitrogen can also be explained by these two suggestions.

Table 1. Oil yield and nitrogen content in Dachengzi shale oil at different heating rates (wt. %, dry ash free basis)

Shale oil sample	Heating rate, ^{o}C min^{-1}	N^{a}_{B}	N^{b}_{N}	N^{c}_{t}	Oil yield
S1	5	0.35	0.53	0.88	14.44
S2	8.5	0.36	0.61	0.97	14.81
S3	12	0.43	0.58	1.01	15.70
S4	20	0.42	0.63	1.05	15.62

[a] basic nitrogen, [b] neutral nitrogen = N_t–N_B, [c] total nitrogen

3.2. Influence of heating rate on basic nitrogen-containing species content in shale oil

3.2.1. The total number of basic nitrogen-containing species

As noted in the literature [20, 23], each compositionally distinct component can be assigned to a definite "class" according to its heteroatomic number. This means that compounds having the same number of heteroatoms are classified into the same class. For example, a compound with an elemental composition $C_cH_hN_nO_oS_s$ is categorized into an "$N_nO_oS_s$" class (the subscripts *n, o* and *s* denote the number of nitrogen, oxygen and sulfur atoms, respectively).

Table 2 presents the total number of the basic nitrogen-containing species identified from the positive-ion FT-ICR mass spectra (Fig. 2) of shale oil

Table 2. The number of basic nitrogen-containing species of each class in Dachengzi shale oil at different heating rates

Shale oil sample	Heating rate, °C min^{-1}	N_1	N_1O_1	N_1O_2	N_1O_3	N_1S_1	N_2	Total
S1	5	747	549	358	393	211	479	2737
S2	8.5	774	549	373	390	237	519	2842
S3	12	787	531	385	409	240	502	2854
S4	20	895	838	416	417	205	583	3354

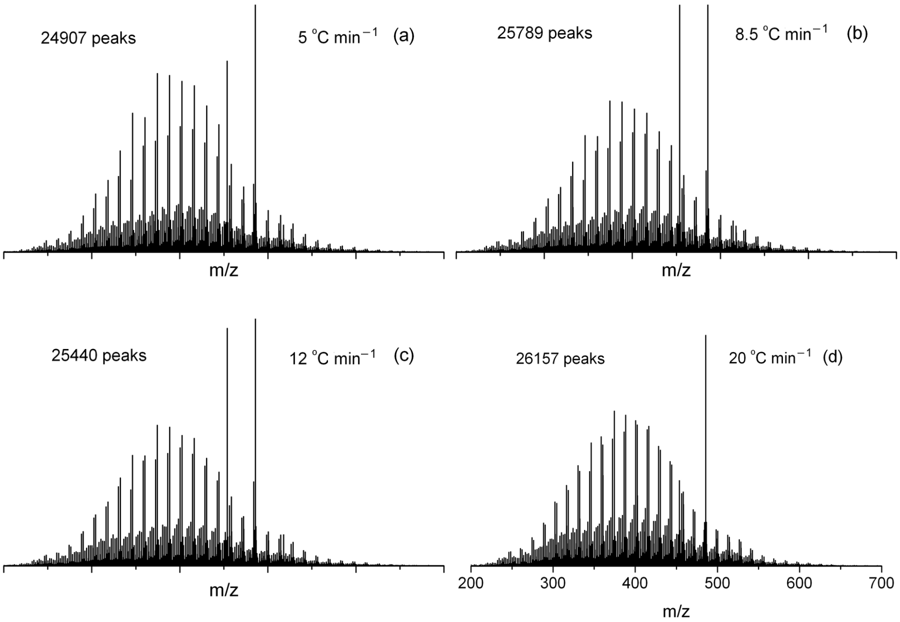

Fig. 2. Broadband positive-ion electrospray ionization FT-ICR mass spectra of Dachengzi shale oil at different heating rates.

samples (S1–S4) at a heating rate ranged from 5 to 20 °C min^{-1}. There is an increase in the number of these basic species, especially N_1, N_1O_1 and N_2 class ones, as heating rate increases. Heating rate influences not only the oil yield but also the composition of the derived oil [32]. Also, Shen *et al.* [33] suggest that there are several different pathways of kerogen decomposition at higher heating rates, which probably results in the increase of the number of these basic species.

3.2.2. The relative abundance of each basic class

Figure 3 shows the relative abundance of the basic classes identified from the positive-ion ESI FT-ICR mass spectra of four samples of shale oil at a heating rate of 5–20 °C min^{-1}. All the oil samples contain six most abundant basic nitrogen-containing classes, including N_1, N_1O_1, N_1O_2, N_1O_3, N_1S_1 and N_2, while N_1 class predominates. Furthermore, in all oil samples, the relative abundance of each basic class does not change when heating rate varies from 5 to 20 °C min^{-1}. However, for each individual class, heating rate affects its relative abundance. As shown in Figure 3, with increasing heating rate the relative abundance of N_1 class decreases while that of the other four classes, namely N_1O_1, N_1O_2, N_1O_3 and N_2, increases.

At lower heating rates, the degree of decomposition of kerogen is higher because the oil shale remains within a given temperature range for a longer period of time [30]. This contributes to the decomposition of more structural units containing nitrogen in oil shale kerogen and to the formation of more nitrogen-containing compounds. On the other hand, lower heating rates generate lower intraparticle gas sweep rates and lead to the degradation of more oil [32], resulting in the transference of more nitrogen present in oil shale into gaseous products instead of shale oil. So, the influence of heating rate on the relative abundance of each basic class includes both positive and negative sides. The relative abundance of N_1 class decreases while that of the other four classes, namely N_1O_1, N_1O_2, N_1O_3 and N_2, increases as heating

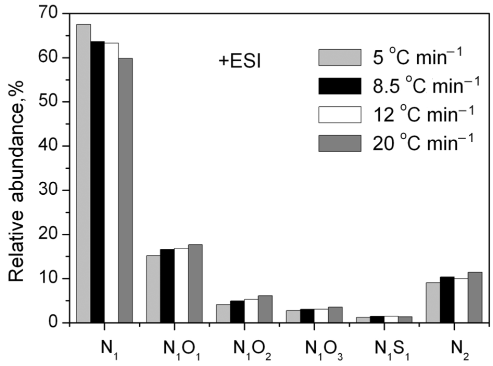

Fig. 3. Relative abundances of basic nitrogen classes identified from the positive-ion ESI FT-ICR mass spectra of Dachengzi shale oil at different heating rates.

rate increases. In case of N_1 class the former factor, i.e. lower heating rate, has a positive effect on its relative abundance, increasing it, while the relative abundance of this class decreases with increasing heating rate.

3.2.3. The relative abundance of each type of N_1, N_1O_1 and N_1O_2 classes

The number of rings plus double bonds (namely double-bond equivalents, DBE) is used to characterize the aromaticity of a compound with an elemental composition and is defined as DBE = $c - h/2 + n/2 + 1$ (for an elemental composition, $C_cH_hN_nO_oS_s$) [20, 23]. The DBE value of a compound is higher if it contains more rings plus double bonds [23]. Again, compounds, which are assigned to the same class if their DBE values are equal, are classified into the same "type".

Figure 4 presents the relative abundance as a function of DBE of N_1, N_1O_1 and N_1O_2 classes identified from the positive-ion ESI FT-ICR mass spectra of four shale oil samples at a heating rate varied from 5 to 20 °C min^{-1}. It can be seen from this figure that these three basic classes have nearly the same DBE range of 4 to 22, which indicates that all the basic species contain 1–6 aromatic rings (including a pyridine ring) according to the rule that

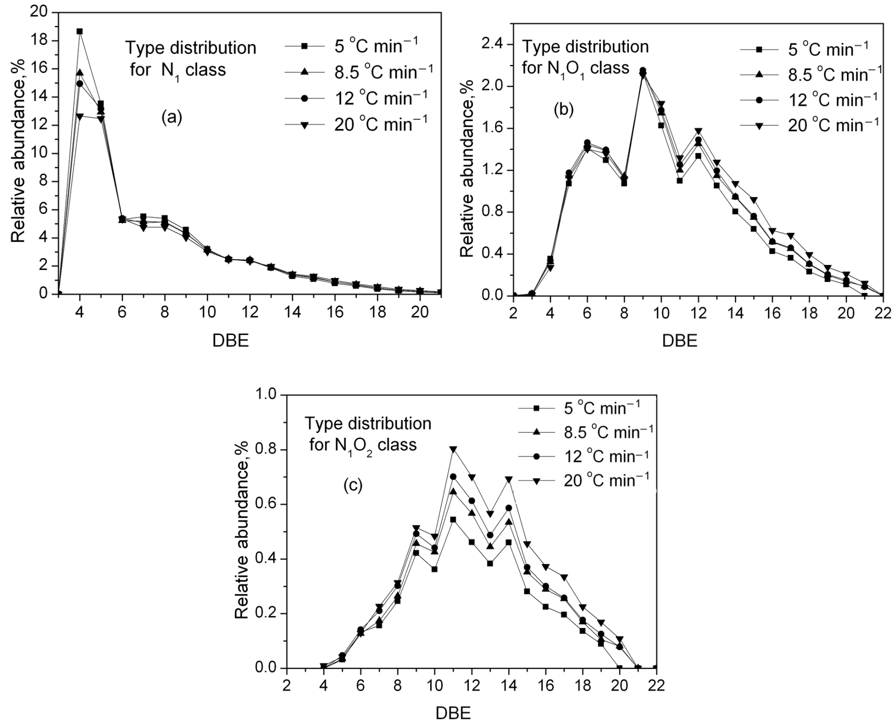

Fig. 4. Type distributions for the three abundant basic classes identified from the positive-ion ESI FT-ICR mass spectra of Dachengzi shale oil at different heating rates.

every increase of three DBE units results in the addition of an additional aromatic ring fused to an aromatic core [26]. Figure 4(a) also demonstrates that for N_1 class species these basic species whose DBE is 4 and 5, namely pyridines and tetrahydroquinolines, have a relative abundance which is far higher than that of other species whose DBE ranges from 6 to 21. This suggests that the major basic nitrogen in shale oil is present as pyridines, which is consistent with results reported by many researchers in the literature [1–4, 9, 26–28]. Furthermore, the relative abundance decreases with increasing DBE value within the whole DBE range of all N_1 class species. The relative abundance as a function of DBE of N_1O_1 and N_1O_2 classes is similar, but that of N_1 class is different and is characterized first by an increase, then a decrease with the increment of DBE value.

Figure 4 also illustrates the influence of heating rate on the relative abundance as a function of DBE of the three classes. For N_1 class it can be observed that with increasing heating rate the relative abundance of species with DBE = 4 (pyridines) undergoes an obvious decrease while that of species with DBE from 5 to 11 experiences a slight decrease. In contrast, the relative abundance of those species, whose DBE ranges from 12 to 22, increases slightly with increasing heating rate. For both N_1O_1 and N_1O_2 classes, the relative abundance increases with increasing heating rate within their respective DBE ranges, particularly, there is a more pronounced increase in the relative abundance within the DBE range of 10–21.

There are several primary pathways for the formation of pyridine-type compounds in shale oil during pyrolysis of oil shale. It is known that part of nitrogen in oil shale kerogen is present as pyridinic structures, which has been determined by X-ray photoelectron spectroscopy (XPS) [34, 35]. Part of pyridinic nitrogen present in kerogen can be directly transformed into the pyridinic type compounds containing a single aromatic ring, or several aromatic rings. For example, many pyridinic type compounds can be produced by rupturing the weak bonds of side chains on the pyridine ring and/or other ring(s) fused to the pyridine ring during pyrolysis, some of which are distributed in shale oil. The secondary reactions occurring during pyrolysis, such as Diels-Alder type, gas-phase cracking or condensation reactions, also involve the formation of mono-aromatic and polycyclic aromatic nitrogen compounds [16].

As stated above, at lower heating rates, oil shale kerogen undergoes a more intensive decomposition due to a longer pyrolysis time within a given temperature range. The fact that the N_1 class species whose DBE ranges from 4 to 11 are more abundant when the heating rate is lower indicates that the formation of these species is mainly controlled by the cracking reactions resulting from the decomposition of kerogen during pyrolysis. Williams and Ahmad suggest that lower heating rates also result in the formation of more carbonaceous residue or more coke via secondary reactions of the liquid oil [32]. Due to their higher boiling point those nitrogen species containing more aromatic rings (DBE = 12–22) probably preferentially participate in the formation of coke or carbonaceous residue. Therefore, it can be suggested that more of those N_1 species (DBE = 12–22) also partake in the formation of more carbonaceous residue or more coke via secondary reactions of the liquid oil and/or the decomposition of kerogen during pyrolysis. Consequently, their relative abundance increases slightly with increasing heating rate.

3.2.4. The relative abundance as a function of carbon number of basic N_1 class species with DBE of 4, 7, 10 and 13

The carbon number, which indicates the degree of alkyl substitution [23], can provide further structural information on nitrogen-containing species. Figure 5 shows the relative abundance as a function of carbon number of basic N_1 class species with DBE of 4, 7, 10 and 13 (i.e. pyridines and their benzalogs containing 1–3 benzene rings). It can be seen from this figure that even though heating rate varies from 5 to 20 °C min^{-1}, the relative abundance of each type of compounds first increases and then decreases with increasing carbon number within their respective whole carbon number ranges. However, when heating rate increases, the relative abundance of pyridines (DBE = 4) and quinolines (DBE = 7) undergoes a relative obvious

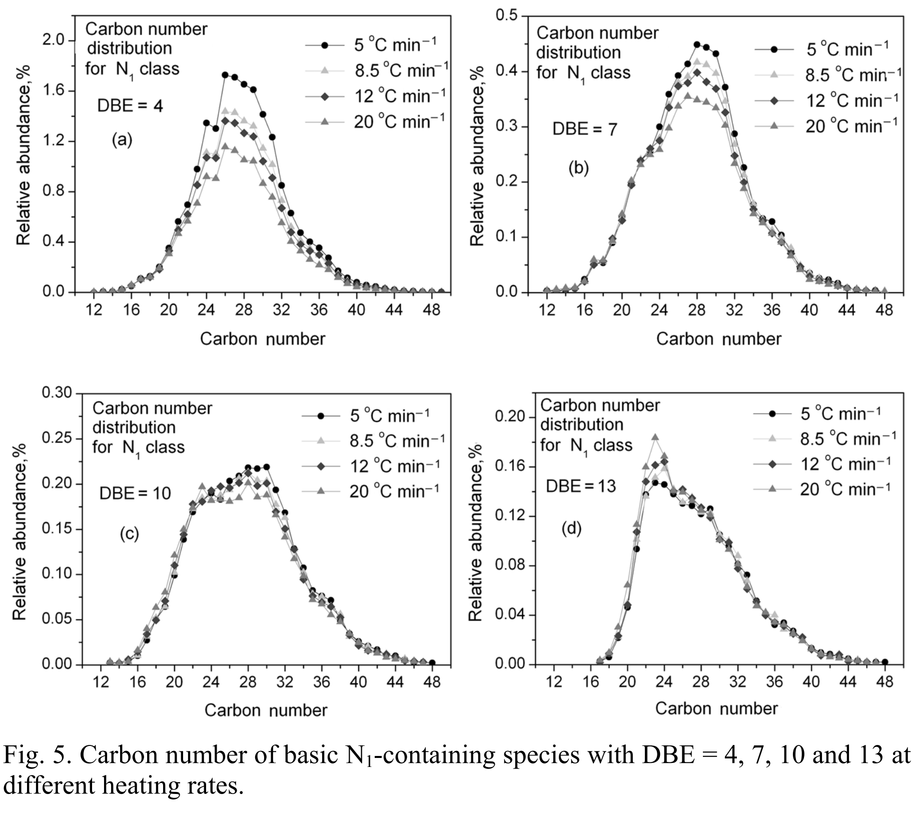

Fig. 5. Carbon number of basic N_1-containing species with DBE = 4, 7, 10 and 13 at different heating rates.

decrease within the carbon number range of 21–37, while there is only a small change in their relative abundance within the carbon number ranges of both 12–21 and 37–48. For those species, whose DBE is 10 and 13, there is also only a slight decrease in relative abundance within the whole carbon number range as heating rate increases.

4. Conclusions

The total and basic nitrogen contents and number of basic nitrogen-containing compounds in Dachengzi shale oil increase with increasing the heating rate from 5 to 20 °C min^{-1}.

All four shale oil samples obtained at different heating rates contain N_1, N_1O_1, N_1O_2, N_1O_3, N_1S_1 and N_2 classes identified from the positive-ion ESI FT-ICR mass spectra, N_1 class being much more abundant than other classes. Furthermore, the relative abundance of each basic class does not change when heating rate varies from 5 to 20 °C min^{-1}.

Heating rate exerts a different effect on each basic class in Dachengzi shale oil. So, N_1 class decreases in relative abundance while N_1O_1, N_1O_2, N_1O_3 and N_2 classes increase as heating rate increases. Moreover, the increased heating rate results in an obvious and slight decrease in the relative abundance of pyridines (DBE = 4) with the highest abundance of N_1 class, and of those whose DBE is within the range of 5–10, respectively. Conversely, the relative abundance of species with DBE over 10 increases slightly. Those N_1O_1 and N_1O_2 class species, whose DBE ranges from 10 to 21, undergo a relative obvious increase in relative abundance as heating rate increases.

As heating rate increases, for pyridines and quinolines (DBE = 7), a relative obvious decrease in relative abundance is mainly observed in those species whose carbon number remains between 21 and 37.

Acknowledgements

The authors wish to thank the State Key Laboratory of Heavy Oil Processing, China University of Petroleum, for providing the 9.4 T ESI FT-ICR MS instrument, and in particular Dr Zhang Yahe for samples analysis and technical advice. This work was supported by the National Natural Science Foundation of China (Grant No. 50906051).

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Presented by J. Qian and V. Oja
Received May 13, 2012