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EXTRACTION AND SPECTROSCOPY ANALYSIS OF BASIC NITROGEN AND PHENOLIC COMPOUNDS OF THE SHALE OIL OF BAOMING OIL SHALE, CHINA

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Abstract. *N,N-Dimethylformamide (DMF) was used as a refining solvent to separate the diesel distillate of shale oil of Baoming oil shale, Xinjiang Province, China. The basic nitrogen and phenolic compounds of the shale oil diesel distillate were first concentrated in the extract oil, then enriched using column chromatography (CC) and thereafter analyzed by Fourier transform infrared spectrometry (FT-IR) and gas chromatography-mass spectrometry (GC-MS). The relative content of the basic nitrogen compounds were increased from 12.09% in the extract oil to 69.50% in the concentrated product by employing the CC method. The relative content of phenolic compounds was increased from 21.55% in the extract oil to 87.57% in the concentrated product. The results showed that the basic nitrogen and phenolic compounds in the diesel distillate of Baoming shale oil could be concentrated and separated gradiently by solvent refining and column chromatography. Sixty basic nitrogen compounds were identified in the concentrated product. Thirty-three phenolic compounds, mainly phenol, alkyl phenol, thymol, naphthol and alkyl naphthol, were identified in the final enriched product. The alkyl phenols consisted mainly of C_1–C_3 phenolic compounds.*

Keywords: *Baoming shale oil, solvent refining, column chromatography, basic nitrogen compounds, phenolic compounds*.

1. Introduction

Shale oil is a product of oil shale low-temperature carbonization. Being for the most part similar to petroleum, it is at the same time rich in nitrogen-, sulfur- and oxygen-containing non-hydrocarbons [1, 2]. On the one hand, the nitrogen and oxygen compounds in shale oil, such as quinoline, aniline, phenol and dimethylphenol, are important raw materials and useful intermediates in industry [3–6]. On the other hand, the nitrogen and phenolic

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compounds present in shale oil have an adverse effect on its processing and utilization [7–10]. Therefore it is necessary to enrich these compounds in order to obtain high-valuable substances prior to the shale oil processing [11–14]. However, before development of chromatographic methods, nitrogen and oxygen compounds were difficult to separate from shale oil without pretreatment [15–17]. Zhu [18] separated shale oils from mountainous area (land) and coastal shelf (sea) oil shale rocks into four fractions by using silica gel column chromatography. The components of each fraction were identified by gas chromatography-mass spectrometry (GC-MS). The results showed that shale oil from land oil shale contained 269 compounds, with abundant hydrocarbon compounds (79%), and some amount of sulfur, oxygen and nitrogen compounds. Shale oil from sea oil shale rock contained 284 compounds, with a high amount of hydrocarbon and oxygen compounds (60% and 29%, respectively). Liang et al. [19] analyzed nitrogen compounds, which had been separated from residue fluid catalytic cracking (RFCC) gasoline by using GC-MS. The main nitrogen compounds identified were anilines, pyridine and quinoline compounds. Employing GC-MS, Guo and Ruan [20] analyzed shale oils obtained from Chinese Fushun oil shale of Liaoning Province and Maoming oil shale of Guangdong Province. The main oxygen compounds identified were phenols, diphenols, alkanones, furans and benzofurans, while phenols constituted 7–8 wt% of oil (< 350 °C).

In this paper, a comprehensive study of the gradient extraction and distribution of the basic nitrogen and phenolic compounds present in the diesel distillate of Xinjiang Baoming shale oil was performed. N,N-Dimethylformamide (DMF) was used to separate shale oil into extract oil and raffinate oil. The basic nitrogen and phenolic compounds were first concentrated in the extract oil. The extract oil was used for the further enrichment of the compounds by employing the column chromatography (CC) method. Finally, the compounds were gradiently concentrated, and then analyzed by Fourier transform infrared spectrometry (FT-IR) and GC-MS.

2. Experimental

2.1. Material

The raw oil used in this study was the fraction 200–360 °C collected from shale oil obtained from Baoming Shale Refinery, Xinjiang Province, China. The properties of the diesel distillate of Baoming shale oil are presented in Table 1.

Table 1. Properties of the diesel distillate of Baoming shale oil

Analysis	Shale oil	Analysis	Shale oil
Density ρ, 20 °C, $g \cdot cm^{-3}$	0.865	Freezing point, °C	–5
Viscosity, 20 °C, $mm^2 \cdot s^{-1}$	5.510	Flash point, °C	65
Carbon residue, wt%	0.780	Nitrogen, wt%	1.003
Basic nitrogen, wt%	0.689	Phenolic compounds, wt%	4.31

2.2. GC-MS and FT-IR analyses

GC-MS analysis was carried out on the Thermo Finnigan Trace DSQ gas chromatograph-mass spectrometer equipped with an HP-35MS capillary column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a flow rate of 1 mL/min. The oven temperature was held at 50 °C for 1 min and then increased to 280 °C at a rate of 2 °C/min for 10 min. The injector temperature was 300 °C. The ion source temperature was maintained at 230 °C, and the ionizing voltage was 70 eV.

FT-IR analysis was carried out on the Thermo Scientific Nicolet iS50 FT-IR spectrometer.

2.3. Experiment methods

2.3.1. Preliminary concentration

Shale oil was pre-concentrated by the method of solvent refining. The basic nitrogen and phenolic compounds were concentrated in the extract oil, as shown in Figure 1.

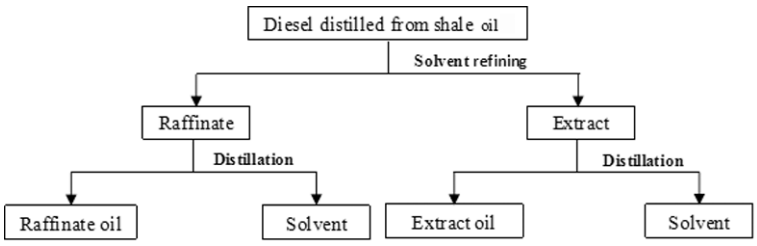

Fig. 1. Preliminary enrichment scheme of the basic nitrogen and phenolic compounds.

2.3.2. Deeper concentration

The extract oil was used for the further enrichment of the basic nitrogen and phenolic compounds. Petroleum ether-benzene/methanol was used as a mobile phase. The components of the raw material could be separated based on their different adsorption abilities with silica gel. The benzene layer solution was obtained by washing the eluent three times with benzene/ methanol. The inorganic layer, which was derived from the benzene layer solution extracted with 3 mol/L HCl, was neutralized with 6 mol/L NaOH. n-Hexane was added to purify the basic nitrogen compounds from the water layer. The compounds were concentrated after distilling the solvent. The organic layer, which was derived from the benzene layer solution extracted with 3 mol/L HCl, was extracted three times with 10% NaOH to yield the inorganic layer. Ether was added to purify the phenolic compounds from the water layer after the inorganic layer was acidified with 6 mol/L HCl. The compounds were concentrated after distilling the solvent, as shown in Figure 2.

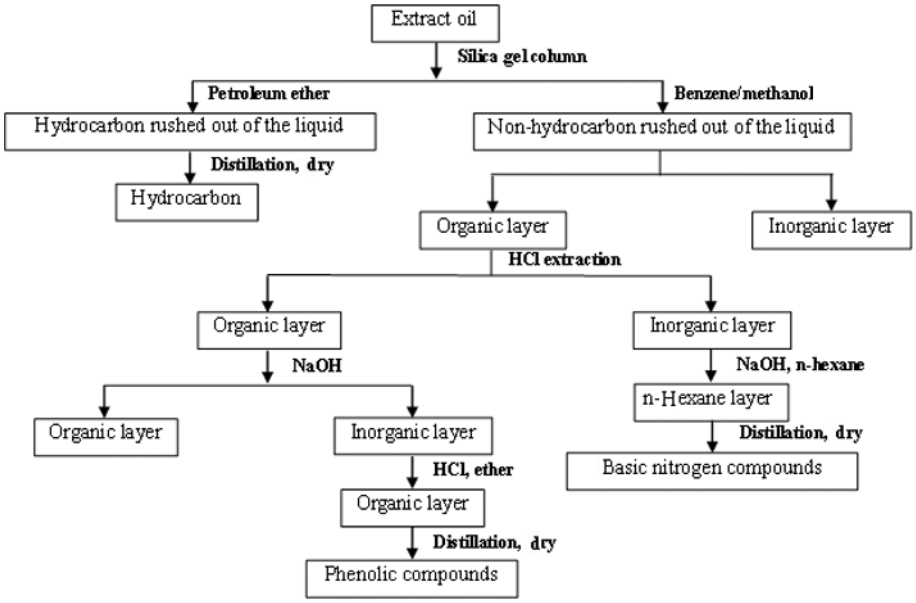

Fig. 2. Deeper enrichment scheme of the basic nitrogen and phenolic compounds.

3. Results and discussion

3.1. Preliminary concentration

Shale oil was concentrated by a physical method in order to retain the structure and composition of the basic nitrogen and phenolic compounds. The solvent refining method was used for preliminary enrichment.

3.1.1. Effect of temperature on the concentration of the basic nitrogen and phenolic compounds

The effect of temperature (50, 60, 70, 80 °C) on the yield of the extract oil and concentration of the basic nitrogen and phenolic compounds at a mass ratio of the extracting agent to oil of 1:1 using DMF as the extracting solvent was investigated, the results are shown in Figures 3 and 4.

As can be seen from Figures 3 and 4, the capacity of DMF to dissolve the basic nitrogen and phenolic compounds was weaker at lower temperatures. The dissolving capacity of DMF was increased as the temperature increased. The contents of basic nitrogen and phenolic compounds in shale oil were the highest at 60 °C. However, the selectivity of the extracting agent decreased as the temperature increased, so the operating temperature should not be too high. The optimal extraction temperature for this study was 60 °C.

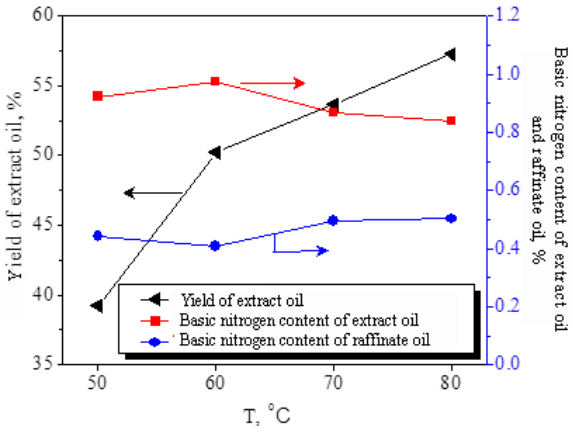

Fig. 3. Effect of temperature on the concentration of basic nitrogen compounds.

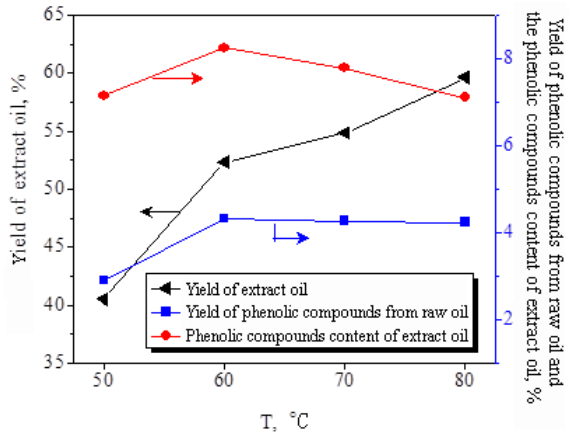

Fig. 4. Effect of temperature on the concentration of phenolic compounds.

3.1.2. Effect of the extracting agent/oil mass ratio on the concentration of basic nitrogen and phenolic compounds

The effect of the extracting agent/oil mass ratio on the yield of extract oil and concentration of the basic nitrogen and phenolic compounds at 60 °C is shown in Figures 5 and 6.

Figures 5 and 6 show that after reaching a balance in DMF, the concentration of basic nitrogen and phenolic compounds in it decreased with increasing solvent dosage at the extraction temperature of 60 °C. Thus, the basic nitrogen and phenolic compounds were transferred to DMF. When the extracting agent/oil mass ratio reached 1, the basic nitrogen and phenolic compounds were concentrated fully. The content of the compounds gradually reduced as the extracting agent/oil mass ratio increased; mean-

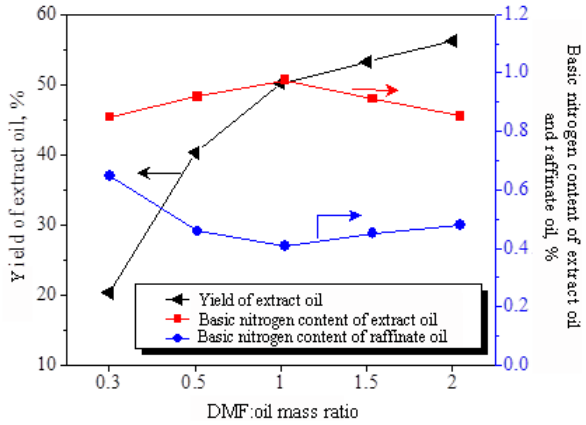

Fig. 5. Effect of the extracting agent/oil mass ratio on the concentration of basic nitrogen compounds.

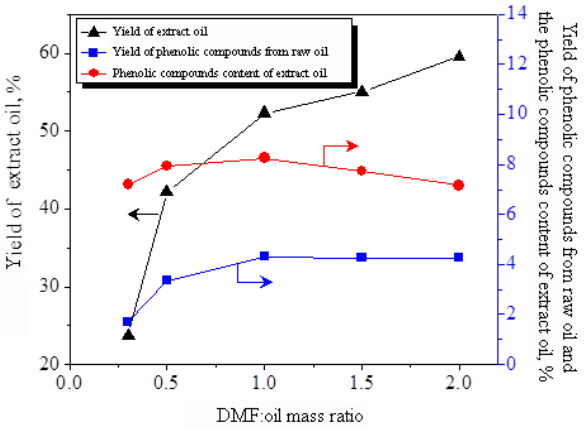

Fig. 6. Effect of the extracting agent/oil mass ratio on the concentration of phenolic compounds.

while, the solvent recovery load and operation cost increased. In this study, the extracting agent/oil mass ratio was chosen to be 1. The yield of the extract oil was 50.21%, and the contents of basic nitrogen and phenolic compounds were 0.975% and 8.25%, respectively.

3.2. Ultra concentration of basic nitrogen compounds

3.2.1. Identification of raw materials for deep enrichment

The extract oil was used for the ultra-enrichment of basic nitrogen and phenolic compounds. The functional groups of the extract oil, the raffinate oil and the diesel distillate of shale oil were detected by FT-IR. The IR spectra of the shale oil diesel distillate and the extract and raffinate oils are

shown in Figure 7. The shale oil diesel distillate and the extract oil were analyzed by GC-MS, the chromatogram is shown in Figure 8.

From Figure 7 it can be seen that all three kinds of oils have a strong peak at 2921 cm^{-1}, which might be caused by the absorption of the C–H vibration absorption on benzene. The peak at 2825 cm^{-1} belongs to the absorption of the C–H vibration of $–CH_3$. The peaks of the extract oil and the shale oil diesel distillate at 1606 cm^{-1} may be assigned to the C=N skeleton vibration on the pyridine ring. This implies the presence of the pyridine ring structure in the extract oil and the shale oil. But at 1606 cm^{-1} there is no obvious peak of the raffinate oil. This indicates that after solvent refining, most materials containing the pyridine ring structure were concentrated in the extract oil. The peaks of the three kinds of oils at 1456 cm^{-1} might be caused by the C=C skeleton vibration on benzene, and is indicative of its existence in the oils. The peaks at 1377 cm^{-1} are attributable to the C–H in-plane bending vibration of $–CH_3$. The two peaks of the extract oil and the diesel distillate of shale oil that appeared at 810 cm^{-1} and 782 cm^{-1}, respectively, were caused by the C–H out-plane bending vibration on benzene.

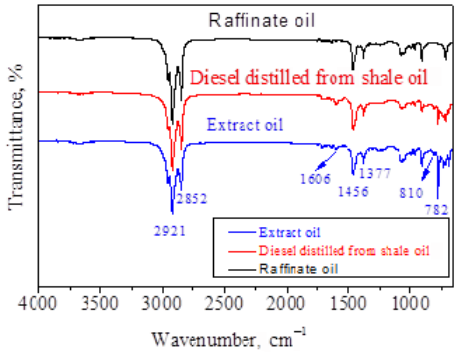

Fig. 7. IR spectra of the diesel distillate of shale oil, the extract oil and the raffinate oil.

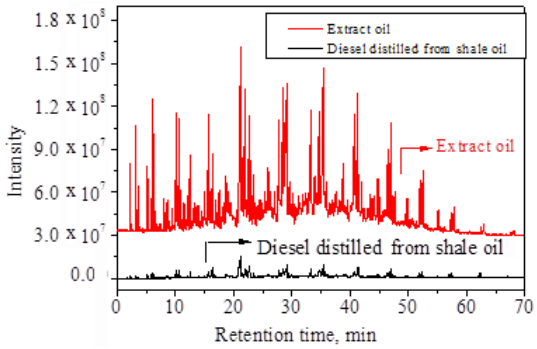

Fig. 8. Chromatogram of the extract oil and the diesel distillate of shale oil.

Figure 8 reveals that the extract oil and the diesel distillate of shale oil are both very complex mixtures. Unlike the shale oil diesel distillate, the nitrogen and phenolic compounds in the extract oil were enriched. Twenty nitrogen compounds and fifteen phenolic compounds were identified in the extract oil by GC-MS. The relative content of nitrogen compounds in the extract oil was 12.71%, while the basic nitrogen compounds accounted for 12.09%. The relative content of phenolic compounds in the extract oil was 21.55%.

3.2.2. Column chromatography separation

Column chromatography method was used as the final enrichment mode for separation of basic nitrogen and phenolic compounds. The basic nitrogen compounds (concentrated product 1) and phenolic compounds (concentrated product 2) obtained from the extract oil were respectively reddish brown and faint yellow in colour, while the former accounted for 16.50% of the extract oil and the latter, 32.00%.

3.3. Identification of basic nitrogen compounds

The basic nitrogen compounds in Baoming shale oil were enriched by extraction and the CC method. The functional groups of the compounds were detected by FT-IR, their IR spectra are shown in Figure 9. The concentrated products were analyzed by GC-MS, the chromatogram is shown in Figure 10.

From Figure 9 it can be seen that there is a broad peak at 3367 cm^{-1}, which may be attributed to the N–H stretching vibration of the basic nitrogen compounds. At the same time, there is a more obvious peak at 1605 cm^{-1}, which belongs to the C=N skeleton vibration on the pyridine ring and indicates the presence of the pyridine ring structure in the compounds. This shows that the basic nitrogen compounds in the diesel distillate of shale oil had been effectively enriched.

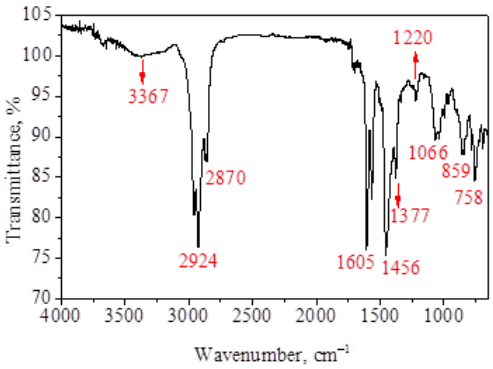

Fig. 9. IR spectra of basic nitrogen compounds.

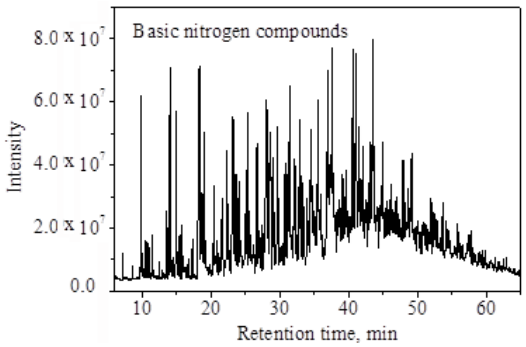

Fig. 10. Chromatogram of the concentrated product 1.

Sixty-eight nitrogen compounds were identified in the concentrated product 1 by GC-MS, their relative content being 74.70%. The contents of different nitrogen compounds in the concentrated product 1 are given in Table 2.

Table 2. Content of basic nitrogen compounds in the concentrated product 1

Nitrogen compound	wt%	Nitrogen compound	wt%
Pyridines	16.53	Naphthalenamine	0.16
Quinolines	25.33	Amides	3.14
Anilines	25.86	Acridine	0.10
Isoquinolinol	1.52	Carbazole	0.73
Indoles	1.33	–	–

Note: "–" represents no data.

The concentrated product 1 contained sixty basic nitrogen compounds, with the relative content of 69.50%. Including mainly benzenamine and alkyl aniline, anilines accounted for 25.86% of the product. Quinolines, which consisted mostly of quinoline, alkyl quinoline, isoquinoline and benzoquinoline, constituted 25.33% of the concentrated product 1.

3.4. Identification of phenolic compounds

The phenolic compounds in Baoming shale oil enriched by extraction and the CC separation method were analyzed by GC-MS, their chromatogram is shown in Figure 11.

Thirty-three phenolic compounds, chiefly phenol, alkyl phenol, thymol, naphthol and alkyl naphthol, were identified in the concentrated product 2 by GC-MS, with the relative content of 87.57%. The contents of different phenolic compounds in the concentrated product 2 are illustratively shown in Figure 12.

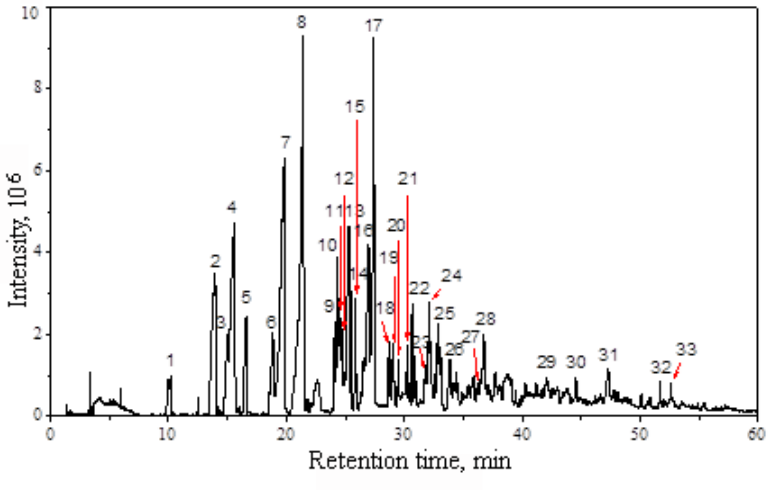

Fig. 11. Chromatogram of phenolic compounds.

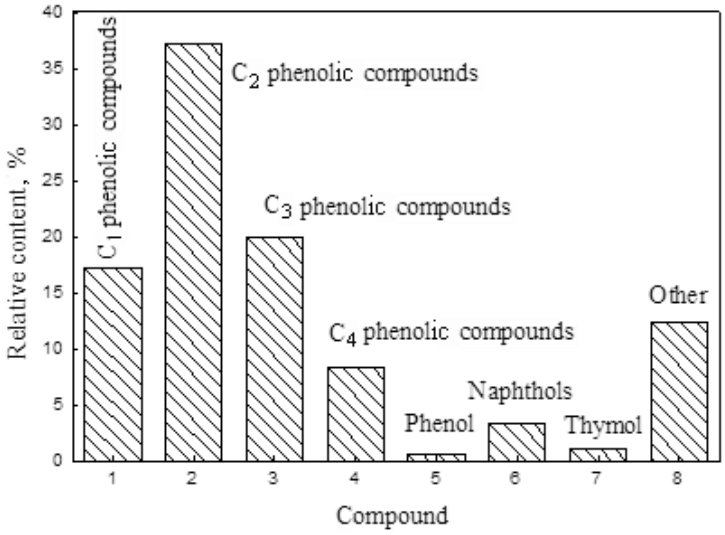

Fig. 12. Content of phenolic compounds in the concentrated product 2.

Of the concentrated product 2, alkyl phenol accounted for 82.55%, of which C_1 phenolic compounds made up 17.18%, C_2 monomers 37.13%, C_3 homologues 19.93% and C_4 monomers 8.32%. Furthermore, phenol made up 0.6% of the concentrated product 2, thymol 1.10% and naphthols 3.32%. So, the phenolic compounds of the extract oil were mainly C_1–C_3 monomers.

4. Conclusions

1. The basic nitrogen and phenolic compounds in the diesel distillate of Baoming shale oil could be enriched and separated using dimethylformamide extraction and column chromatography. The content of basic nitrogen compounds was increased from 12.09% in the extract oil to 69.50% in the concentrated product 1. The content of phenolic compounds was increased from 21.55% in the extract oil to 87.57% in the concentrated product 2.
2. Sixty basic nitrogen compounds, mostly benzenamine, alkyl aniline, quinolones and pyridines, were identified in the final enriched product, their relative content in the product being 69.50%. Among the basic nitrogen compounds, anilines and quinolines were the major ones. Of the final enriched product, anilines accounted for 25.86% and quinolines 25.33%.
3. Thirty-three phenolic compounds, predominantly phenol, alkyl phenol, thymol, naphthol and alkyl naphthol, were identified in the final enriched product. Alkyl phenols consisted mostly of C_1–C_3 phenolic compounds, of which C_1 monomers accounted for 17.18%, C_2 homologues 37.13% and C_3 monomers 19.93%.

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