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Characterization of Middle-Temperature Gasification Coal Tar. Part 1: Bulk Properties and Molecular Compositions of Distillates and Basic Fractions

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ABSTRACT: A middle-temperature coal tar (MTCT) was distilled into multiple narrow boiling point fractions. The MTCT and its distillate fractions were subjected to bulk property analysis and molecular compositional characterization by gas chromatography–mass spectrometry. Acid/basic liquid extraction was performed to separate the MTCT into acidic, basic, and neutral fractions, which were characterized by positive-ion electrospray ionization (ESI) Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry. The dominant compounds in MTCT were aromatics, phenols, and normal alkanes. The number of carbon atoms in the substituent chains varied over a relatively broad range for each homology. The composition of narrow distillate fractions varied: light naphtha (<100 °C) had a high benzene content, which is an unsuitable gasoline blending stock; middle distillates (160–240 °C) enriched with phenols, which is a good extraction feedstock for chemical products; and heavy distillates (>240 °C) are a hydrotreating feedstock for clean fuel production. The MTCT had large amounts of acidic and basic components, consisting of oxygen- and nitrogen-containing molecules. The basic fraction accounted for 2.68 wt % MTCT. Only nitrogen compounds in the MTCT could be detected by positive-ion ESI. Most of the oxygen-containing molecules exhibited a weak acidity and were partially extracted into the acidic fraction. Basic nitrogen compounds co-existed in the acidic, basic, and neutral fractions of MTCT. However, the molecular compositions of basic nitrogen compounds were different among these fractions: molecules with low carbon numbers and high aromaticities were found in the acidic and basic fractions, whereas mono-nitrogen basic compounds were abundant in the neutral fraction.

1. INTRODUCTION

In China, coal plays a vital role in the chemical industry, particularly in the production of methanol, olefins, aromatics, and ammonia/urea. With abundant coal reserves and a soaring demand for consumer products, the coal-based chemical industry in China has grown substantially. Coal tar (CT) is a byproduct from coal carbonization and gasification processes. On the basis of processing temperature, CT is classified as low-temperature (650 °C), middle-temperature (800 °C), and high-temperature coal tars (1000 °C).^{1–3} From a broad perspective, low-temperature coal tar (LTCT) and middle-temperature coal tar (MTCT) are commonly referred to as LTCT, because of their similar molecular compositions.³ LTCT is a potential feedstock for chemical products and transportation fuels. Hence, it is important to better understand the composition of LTCT for downstream processing and reducing environmental impacts of process operation. The chemical composition of LTCT is distinctly different from that of high-temperature coal tar.^{4–6} LTCT has been a supplementary feedstock to petroleum crude oil since the 1970s.^{7–9} Tremendous efforts have been devoted to characterize the molecular structure and mass distribution of coal-derived liquids. Size-exclusion chromatography (SEC)¹⁰ is commonly used to determine the molecular size distributions of complex coal-derived liquids. Nuclear magnetic resonance (NMR),¹¹ X-ray absorption near edge structure (XANES),¹² X-ray photoelectron spectroscopy (XPS) analysis,¹³ and Fourier transform infrared (FTIR) spectroscopy have been used to

identify functional groups and determine the ratio of aromatics/saturates in coal-derived liquids.¹⁴ Gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS) have been used to determine the molecular components of coal-derived liquids.^{15–19} However, because of the complexity and structural similarity of the compounds in LTCT, chromatographic peaks of various compounds overlap. Moreover, these conventional analytical techniques are inadequate to identify polar heteroatom compounds. The electrospray ionization Fourier transform ion cyclotron resonance mass spectrometry (ESI FT-ICR MS) has been successfully used to characterize the coal tar and extracts. The results show that ESI FT-ICR MS is an effective analytic tool for coal-derived liquids.^{20–22} LTCT consists of aliphatic and aromatic hydrocarbons and oxygen- and nitrogen-containing heteroatom compounds.^{7,23} The high amount of oxygen-containing compounds is the key characteristic composition of LTCT. The abundant oxygen-containing compounds in LTCT are phenols, indanols, naphthanol, and biphenols.^{18,24,25} Shi et al.²⁶ identified dihydroxy compounds in LTCT, which contained an aromatic core structure of benzene, indane, biphenyl (and/or acenaphthene), naphthalene, fluorenes, and phenanthrenes (and/or anthracenes). These oxygen-containing compounds are highly selective to be ionized by ESI

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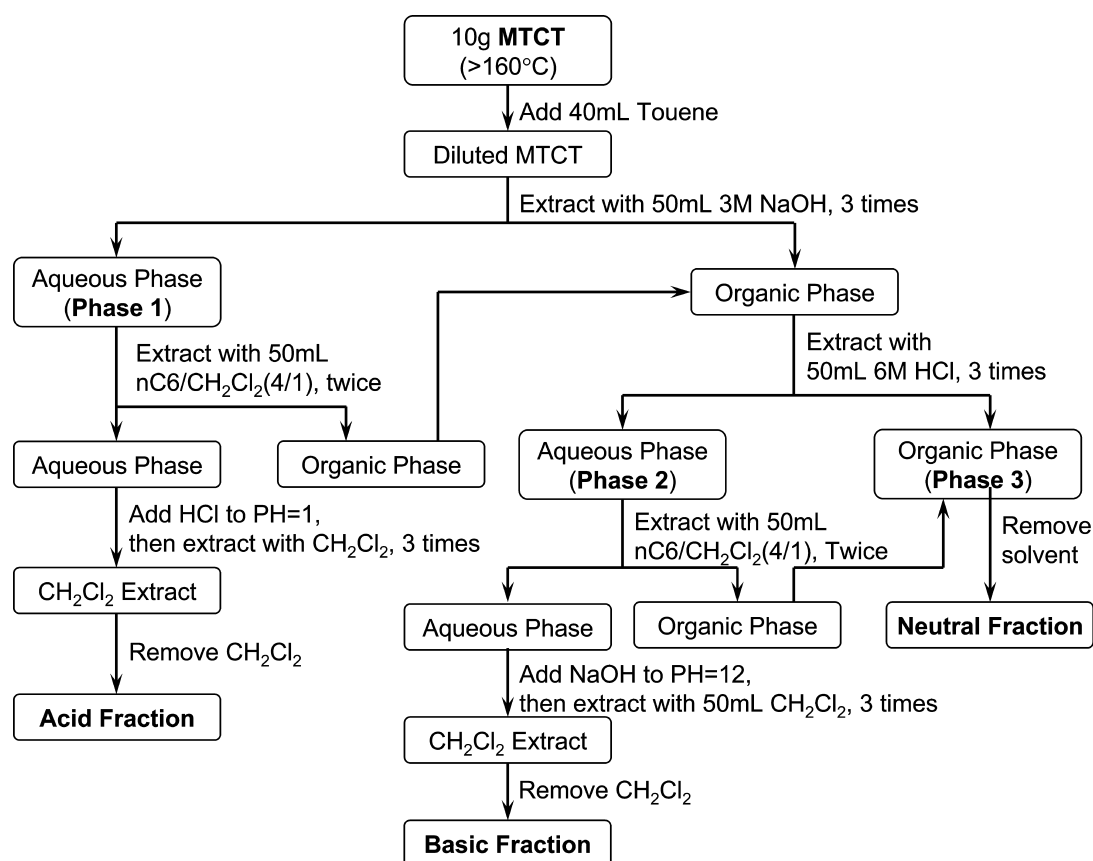


Figure 1. Acidic/basic extraction scheme for MTCT.

in the negative-ion mode. From our recent analytical work on coal-derived products, a series of papers on molecular compositions of MTCT and LTCT will be presented. In this paper, a MTCT and its narrow distillate fractions were characterized for their bulk properties and molecular compositions. The MTCT was also subjected to acidic/basic liquid separation to prepare the acidic, basic, and neutral fractions. The MTCT basic fraction was characterized by GC–MS and positive-ion ESI FT-ICR MS.

2. EXPERIMENTAL SECTION

2.1. Materials. Three liquid products, naphtha, middle oil, and tar, were obtained from a commercial Lurgi lignite gasification plant. The temperature gradient of the gasification reaction zone varied from 1100 to 550 °C. The operating pressure of the gasification plant was 3.1 MPa. The three gasification products, namely naphtha, middle oil, and tar were blended according to their yield ratios to yield a MTCT sample.

2.2. Dewatering of the MTCT Sample. The true boiling point distillation was performed using a FS-II distillation instrument equipped with a column with 15 theoretical plates and a 10:1 reflux ratio. A total of 5 L of MTCT was loaded into the distiller. The distillation was carried out under atmospheric conditions from room temperature to 110 °C. Because water and naphtha were azeotropic, they were distilled, condensed, and collected in the side bulb of the distiller. After the water/naphtha mixture settled for 0.5 h, water and naphtha were segregated into two distinct phases. Water was decanted. Naphtha was obtained and added to the MTCT that remained in the distiller. The dewatered MTCT sample was used in the subsequent tests and analyses.

2.3. Distillation. Distillation was resumed on the water-free MTCT sample. The first distillate fraction collected was up to 80 °C. Six sequential distillate fractions were collected at 80–200 °C in 20 °C increments. After that, the distiller was subjected to a 10 mmHg vacuum. The vacuum distillation temperatures were converted to the atmospheric true boiling point (TBP) temperatures using the American

Table 1. Properties of MTCT

density at 20 °C (g/cm ³)	0.9689
viscosity at 20 °C (mm ² /s)	14.6
viscosity at 50 °C (mm ² /s)	3.4
freezing point (°C)	7
flash point (°C)	4
CCR (wt %)	3.5
ash (wt %)	0.03
carbon (wt %)	85.02
hydrogen (wt %)	8.98
H/C (atomic ratio)	1.27
oxygen (wt %)	4.37
sulfur (wt %)	0.33
nitrogen (wt %)	0.67

Petroleum Institute (API) 5A1.13 method. Sequential distillate fractions were collected from the TBP at 200 to 400 °C in 20 °C increments. All of the MTCT distillate fractions were kept in brown glass bottles wrapped by silver wrapping paper, which were blanketed with nitrogen gas before the bottles were capped. The MTCT samples were kept in a cooler at 4 °C.

2.4. Acidic/Basic Extraction. The topped MTCT sample was obtained by removing the volatile compounds of the dewatered MTCT sample, which were less than 160 °C by distillation. The topped MTCT sample was subjected to liquid extraction to prepare acidic, basic, and neutral fractions. The acidic/basic liquid extraction scheme is shown in Figure 1. A total of 10 g of topped MTCT was dissolved in 40 mL of toluene. The diluted MTCT mixture was extracted with 50 mL of 3 M sodium hydroxide (NaOH) solution 3 times to yield an aqueous phase (phase 1) and an organic phase. The organic phase was extracted with 50 mL of 6 M hydrochloric acid (HCl) solution 3 times to yield an aqueous phase (phase 2) and an organic phase (phase 3). Phase 1 in a beaker was immersed in an ice bath and added dropwise with 6 M HCl solution.

The solution mixture was stirred continuously, and the solution acidity was determined by pH paper. When the mixture solution pH was 1, the solution was extracted with 50 mL of dichloromethane (CH_2Cl_2) 3 times, followed by solvent evaporation using a rotary evaporator to yield the acidic fraction (AF). A similar titration procedure was applied to phase 2 with 3 M NaOH solution to yield the basic fraction (BF). The neutral fraction (NF) was obtained from phase 3 after solvent evaporation, which was combined with the organic phase of phase 2. The yields of AF, NF, and BF were 25.47, 69.92, and 2.68 wt %, respectively.

2.5. GC and GC–MS Analysis. GC analysis was carried out on a Agilent 7890 equipped with a HP-5 capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$) and a flame ionization detector (FID). The injector and detector were both set at a temperature of $300\text{ }^\circ\text{C}$. Nitrogen was used as

a carrier gas in a following rate of 1 mL/min . The oven was held at $40\text{ }^\circ\text{C}$ for 10 min, increased at a rate of $4\text{ }^\circ\text{C/min}$ to $300\text{ }^\circ\text{C}$, and held constant for 15 min. Thermo-Finnigan Trace DSQ GC–MS was used to analyze the compositions of MTCT and its basic fractions. GC–MS was equipped with a HP-5 MS capillary column ($30\text{ m} \times 0.25\text{ mm} \times 0.25\text{ }\mu\text{m}$). GC operation parameters were the same as the GC–FID analysis, except the helium carrier gas. The GC–MS interface and MS ion source were both at $250\text{ }^\circ\text{C}$, with MS working at 70 eV of electron energy with a $300\text{ }\mu\text{A}$ ion current and a scan from 35 to 500 atomic mass units (amu) in each 0.5 s.

2.6. FT-ICR MS Analysis. Bruker apex-ultra FT-ICR MS was used to analyze the basic nitrogen compounds in MTCT, AF, BF, and NF. MS was equipped with a 9.4 T superconducting magnet. The sample was dissolved in methanol/toluene (1:1, v/v), and then the sample solution was diluted with a solvent mixture of toluene/methanol (1:3) to 0.02 mg/mL . The ESI source was operated in the positive mode. The emitter voltage was -3.5 kV . The capillary column front end voltage was -4.0 kV . The capillary column end voltage was -320 V . The ion-accumulated time was 0.01 s, and time-of-flight window was 1 ms. The mass range was set at m/z 100–600. The data size was set to 4 M words. A total of 64 scans were accumulated. Methodologies for FT-ICR MS mass calibration, data acquisition, and processing have been described elsewhere.^{27,28}

Table 2. Yields and Physical Properties of the Distillates

	boiling point ($^\circ\text{C}$)	yield (wt %)	cumulative weight (%)	density at $20\text{ }^\circ\text{C}$ (g/cm^3)	viscosity (mm^2/s)	molecular weight
1	IBP–80	4.16	4.16	0.7700		
2	80–100	4.01	8.17	0.8293		
3	100–120	5.32	13.49	0.8259		
4	120–140	1.82	15.31	0.8144		
5	140–160	3.03	18.34	0.8282		
6	160–180	4.79	23.13	0.8683		
7	180–200	4.76	27.89	0.9167	1.51	
8	200–220	4.23	32.12	0.9542	1.81	341
9	220–240	9.79	41.91	0.9590	2.44	353
10	240–260	3.16	45.07	0.9661	2.97	413
11	260–280	2.62	47.69	0.9774	3.74	425
12	280–300	4.21	51.90	0.9875	4.81	437
13	300–320	4.76	56.66	0.9998	8.12	442
14	320–340	5.33	61.99	1.0162	12.82	487
15	340–360	3.66	65.65	1.0125	23.56	477
16	360–380	9.19	74.84	1.0269	33.33	486
17	380–400	4.24	79.08	1.0240	136.9	497
18	>400	18.07	97.15			

3. RESULTS AND DISCUSSION

3.1. Bulk Properties of MTCT and Its Subfractions. The properties of MTCT are listed in Table 1. The MTCT was a low-viscosity liquid and contained a large amount of light naphtha, which was condensed and collected in the cryogenic separation process. The density of MTCT was similar to that of heavy petroleum crude oil; however, the H/C ratio of MTCT (1.27) was lower than that of heavy petroleum crude oil (1.4–1.7).²⁹ The freezing point ($7\text{ }^\circ\text{C}$) of MTCT was slightly higher than the flash point ($4\text{ }^\circ\text{C}$). This implies that the molecules of MTCT were with a large dispersion, i.e., large molecules with a high freezing point and small volatile molecules with a low flash point. The Conradson carbon residue (CCR) and ash contents of MTCT were relatively low compared to those of

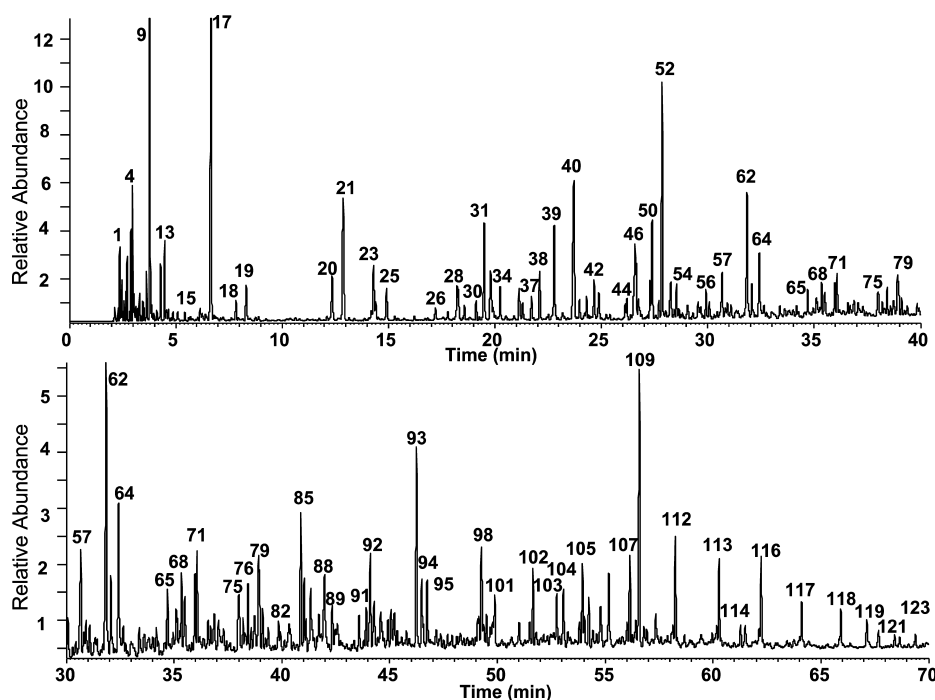


Figure 2. Total ion chromatograms of the MTCT.

Table 3. Compounds Identified in the MTCT

peak number	retention time, Rt (min)	compounds	area percent (%) ^a	peak number	retention time, Rt (min)	compounds	area percent (%) ^a
1	2.37	<i>n</i> -pentane	0.68	60	30.92	C ₃ -phenol	0.31
2	2.72	isohexane	0.48	61	31.09	C ₃ -phenol	0.25
3	2.89	1-hexene	0.61	62	31.85	2-methylnaphthalene	2.61
4	2.97	<i>n</i> -hexane	0.92	63	32.07	<i>n</i> -tridecane	0.54
5	3.29	cyclohexane	0.24	64	32.42	1-methylnaphthalene	1.41
6	3.46	5-methyl-1,3-cyclopentene	0.15	65	34.69	diphenyl	0.53
7	3.52	1-methyl-1,3-cyclopentene	0.13	66	35.10	C ₂ -naphthalene	0.35
8	3.62	1-methyl-1-cyclopentene	0.48	67	35.15	C ₂ -naphthalene	0.22
9	3.78	benzene	13.01	68	35.35	C ₂ -naphthalene	0.57
10	3.86	thiophene	0.17	69	35.51	<i>n</i> -tetradecane	0.60
11	4.11	cyclohexene	0.11	70	35.97	C ₂ -naphthalene	0.61
12	4.29	1-heptene	0.68	71	36.08	C ₂ -naphthalene	0.74
13	4.48	<i>n</i> -heptane	0.89	72	36.58	C ₂ -naphthalene	0.27
14	5.09	methylcyclohexane	0.15	73	36.69	C ₂ -naphthalene	0.21
15	5.43	C ₂ -cyclopentane	0.11	74	37.29	C ₂ -naphthalene	0.25
16	6.15	heptene	0.21	75	38.01	acenaphthene	0.74
17	6.65	toluene	8.45	76	38.43	<i>n</i> -pentadecane	0.46
18	7.83	1-octene	0.39	77	38.58	C ₃ -naphthalene	0.18
19	8.31	<i>n</i> -octane	0.73	78	38.73	dibenzofuran	0.45
20	12.35	ethylbenzene	1.06	79	38.92	naphthol	0.91
21	12.86	xylene	3.12	80	39.11	C ₃ -naphthalene	0.31
22	14.20	styrene	0.21	81	39.84	C ₃ -naphthalene	0.24
23	14.30	xylene	1.15	82	39.92	C ₃ -naphthalene	0.17
24	14.40	<i>n</i> -nonene	0.36	83	40.33	C ₃ -naphthalene	0.35
25	14.91	<i>n</i> -nonane	0.68	84	40.40	C ₃ -naphthalene	0.18
26	17.20	C ₁₀ H ₂₂	0.27	85	40.88	fluorene	1.09
27	17.79	C ₃ -benzene	0.17	86	41.04	C ₃ -naphthalene	0.56
28	18.22	C ₃ -benzene	0.66	87	41.34	<i>n</i> -hexadecane	0.63
29	18.28	C ₃ -benzene	0.57	88	41.98	methyldibenzofuran	0.95
30	18.56	C ₃ -benzene	0.25	89	42.34	methyldibenzofuran	0.42
31	19.49	phenol	2.49	90	42.57	methyldibenzofuran	0.24
32	19.79	C ₃ -benzene	1.24	91	43.92	methylfluorene	0.36
33	19.91	C ₁₀ H ₂₀	0.25	92	44.11	<i>n</i> -heptadecane	0.88
34	20.24	<i>n</i> -decane	0.59	93	46.25	phenanthrene	1.63
35	21.14	C ₃ -benzene	0.60	94	46.49	anthracene	0.54
36	21.30	C ₄ -benzene	0.34	95	46.74	<i>n</i> -octadecane	0.54
37	21.71	indane	0.41	96	49.09	3-methylphenanthrene	0.21
38	22.10	indene	0.89	97	49.14	2-methylphenanthrene	0.21
39	22.78	<i>o</i> -cresol	1.80	98	49.26	<i>n</i> -nonadecane	0.92
40	23.71	<i>m</i> -/ <i>p</i> -cresol	3.86	99	49.49	methylanthracene	0.27
41	23.98	1-undecene	0.38	100	49.67	9-methylphenanthrene	0.21
42	24.65	<i>n</i> -undecane	0.74	101	49.88	1-methylphenanthrene	0.48
43	24.88	C ₄ -benzene	0.67	102	51.65	<i>n</i> -eicosane	0.60
44	26.13	C ₂ -phenol	0.32	103	52.75	C ₂ -phenanthrene	0.46
45	26.20	C ₂ -phenol	0.35	104	53.06	fluoranthene	0.59
46	26.58	C ₂ -phenol	1.90	105	53.94	<i>n</i> -heneicosane	0.64
47	26.64	C ₂ -phenol	0.87	106	54.03	pyrene	0.24
48	26.75	C ₂ -phenol	0.38	107	56.14	<i>n</i> -docosane	0.71
49	27.29	C ₂ -phenol	0.63	108	56.25	benzofluorene	0.54
50	27.39	C ₂ -phenol	1.75	109	56.58	retene	0.21
51	27.71	C ₂ -phenol	0.31	110	56.80	methylpyrene	0.11
52	27.85	naphthalene	4.18	111	56.93	methylpyrene	2.31
53	28.27	C ₂ -phenol	0.96	112	58.25	<i>n</i> -tricosane	0.21
54	28.54	<i>n</i> -dodecane	0.54	113	60.28	<i>n</i> -tetracosane	0.15
55	29.55	C ₃ -phenol	0.42	114	61.28	benzo(<i>a</i>)anthracene	0.85
56	29.91	C ₃ -phenol	0.54	115	61.49	chrysene	0.67
57	30.07	C ₃ -phenol	0.35	116	62.23	<i>n</i> -pentacosane	0.18
58	30.68	C ₃ -phenol	1.12	117	64.11	<i>n</i> -hexacosane	0.25
59	30.82	C ₃ -phenol	0.22	118	65.93	<i>n</i> -heptacosane	0.73

Table 3. continued

peak number	retention time, Rt (min)	compounds	area percent (%) ^a	peak number	retention time, Rt (min)	compounds	area percent (%) ^a
119	67.13	benzofluoranthene	0.38	122	68.66	benzo(<i>a</i>)pyrene	0.20
120	67.69	<i>n</i> -octacosane	0.32	123	69.38	<i>n</i> -nonacosane	0.11
121	68.42	benzo(<i>e</i>)pyrene	0.25				

^aThe peak area percent was normalized by individual peak area/total peak area of 123 peaks.

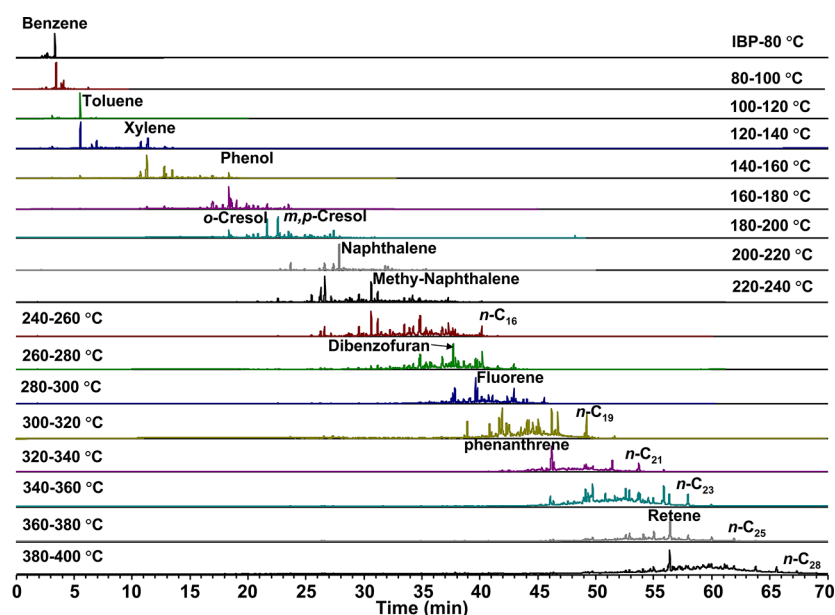


Figure 3. Total ion chromatograms of narrow MTCT distillates.

high-temperature coal tars or petroleum-derived vacuum residua. Because the feedstocks with high CCR and ash contents cause rapid catalyst deactivation and fouling problems in refining operations, the low CCR and ash contents of MTCT indicated that MTCT is a good candidate refinery feedstock. As expected, the coal-derived MTCT had a high oxygen content. The low sulfur content of MTCT is also favorable for clean fuel production. However, the high nitrogen content of MTCT may require more extensive processing. The nitrogen compounds in MTCT should warrant more detailed investigation. Table 2 shows the yield and physical properties of MTCT distillate fractions. The yield of each fraction was relatively constant at 4 wt %, except for 120–140 °C, 220–240 °C, and 360–380 °C fractions. The yields according to the boiling point temperature of petroleum products were as follows: naphtha (lower than 200 °C), 27.9 wt %; middle distillates (200–340 °C), 34.1 wt %; and atmospheric residues (higher than 340 °C), 38.1 wt %. As expected, the values of the density, viscosity, and molecular weight increased with the distillate boiling point temperature.

3.1.1. Compositions of MTCT and Its Narrow Distillate Subfractions. The total ion chromatograms of MTCT are shown Figure 2. A total of 123 compounds were identified in MTCT and listed in Table 3. The retention times and peak area were ranged from a parallel run with GC–FID. The chromatogram in Figure 2 showed that MTCT had three dominant groups of compounds: aromatics, phenols, and saturates. The aromatics were mainly 1–4 aromatic-ring compounds with and without short side chains. The abundant aromatic compounds were benzene and toluene, followed by naphthalene. The abundant phenolic compounds were alkyl

phenols. Although indanols, naphthanols, and dihydric phenol were also identified by MS, quantitative analyses of these compounds were difficult because of the overlapping of chromatogram peaks. The detailed characterization of phenolic compounds will be discussed in our future publication. The MTCT had a relatively high amount of normal paraffins compared to high-temperature coal tars and pyrolyzed petroleum products. The presence of normal distribution yields of phenols and long alkyl normal paraffins ranging from C5 to C30 suggested that the MTCT was produced in a relatively low-severity process condition. Otherwise, these relatively large paraffinic compounds would be pyrolyzed into smaller molecules and/or with desorption of phenol groups.

Figure 3 shows the total ion chromatograms of narrow MTCT distillate fractions. The peak retention time was shifted from short to long as the distillate boiling point temperature increased. An increased overlapping of chromatogram peaks in adjacent fractions indicated that the separation of compounds by distillation was inadequate to isolate individual compounds. Nevertheless, the narrow distillate fractions were adequate for GC–MS analysis. Benzene, toluene, and xylenes (BTX) were dominant compounds in the distillate fractions below 160 °C. Phenol was in the 140–180 °C distillate fractions. Phenol and methyl phenols were in the 180–200 °C distillate fraction. Phenols, naphthalene, and its homologues were in the 200–220 °C distillate fraction. A complex mixture of dibenzofuran, alkyl naphthalene, fluorene, and biphenyl compounds were in the 260–280 °C distillate fraction. Fluorenes were in the 280–300 °C distillate fraction. Alkyl fluorenes and alkyl naphthols, phenanthrene,

octadecane, and nonadecane were in the 300–320 °C distillate fraction. Alkanes and phenanthrenes were in the 320–340 °C distillate fraction. The compounds in the 340 °C+ fractions were more complex; some long-chain alkanes and retene could be observed in the chromatogram. Because the MTCT naphtha (<160 °C) contained a large amount of BTX, it is a suitable feedstock for chemical production. The high benzene content precludes MTCT naphtha from gasoline production. The MTCT middle distillates (160–240 °C) were enriched with phenols, which should be removed before the middle distillates are subjected to refining operations. The MTCT heavy fraction contained highly complex compounds, which are difficult to separate. Hence, hydrotreating of the MTCT heavy fraction is the preferred processing step for clean fuel production.

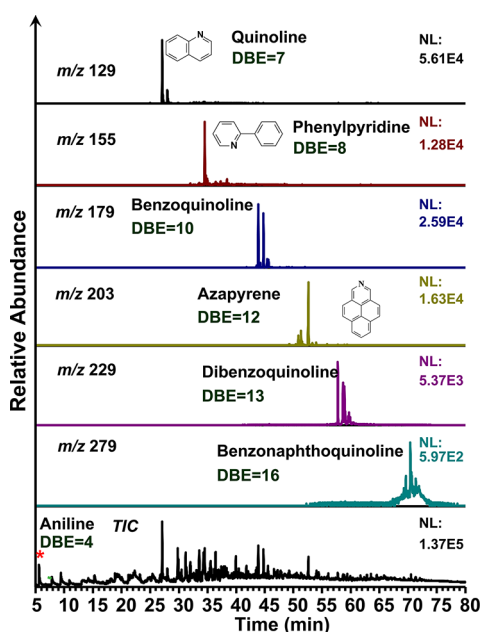


Figure 4. Mass chromatograms of MTCT BFs.

3.2. Characterization of the BF by GC–MS. The BF accounted for 2.68 wt % MTCT, which was much less than that of the AF. However, the amount of BF was much more than that derived from petroleum crude (typically less than 1 wt %). The mass chromatograms of BF subfractions were shown in Figure 4. There was a huge hump with an irregular edge in the total ion chromatogram from 12.5 to 80 min, indicating a complex composition of the analyte. In addition, peak trailing enhanced the peak overlapping. MS is adequate in identifying each compound; e.g., quinoline and isoquinoline were clearly identified in the m/z 129 mass chromatogram. Phenylpyridine, benzoquinoline, azapyrene, dibenzoquinoline, and benzonaphthoquinoline were tentatively identified in the mass chromatograms of m/z 155, 179, 203, 229, and 279, respectively. Mass spectra showed that all of the separate peaks corresponded to basic nitrogen compounds. Without calibration with standard compounds or credible retention index references, it would be ambiguous to identify the structures of these heteroatom compounds. Furthermore, it is impossible to separate and identify all of the individual compounds in the BF, as well as other complex fossil fuel products. A feasible approach is to characterize the compounds based on their molecular compositions by MS, which is a promising way for the “petroleomics”^{30,31} application.

3.3. Characterization of Basic Nitrogen Compounds by Positive-Ion ESI FT-ICR MS. Because the basic nitrogen compounds can be selectively ionized by positive-ion ESI, they can be characterized using FT-ICR MS. Separating the MTCT into acidic, basic, and neutral fractions would enhance the analysis dynamic range of FT-ICR MS. However, the yield and purity of basic compounds are two objectives that could not be achieved synchronously. To perform a thorough characterization of basic nitrogen compounds, the MTCT and its acidic, basic, and neutral fractions were characterized by positive-ion ESI FT-ICR MS.

Figure 5 shows the broad-band positive-ion ESI FT-ICR MS mass spectra of the MTCT and its subfractions. Mass-scale-expanded spectra at m/z 314 and 414 were shown in Figures 6 and 7, respectively. In theory, the mass spectrum of BF

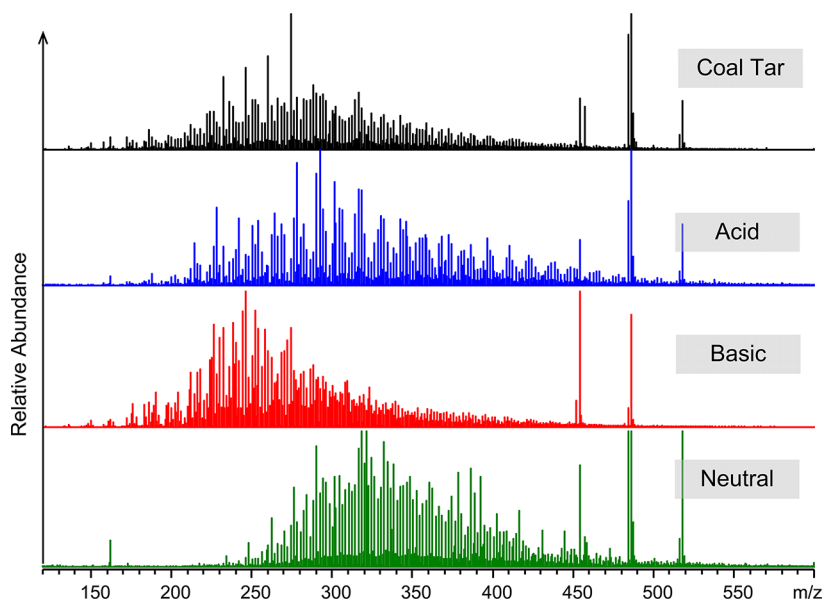


Figure 5. Broad-band positive-ion ESI FT-ICR MS spectra of MTCT and its subfractions.

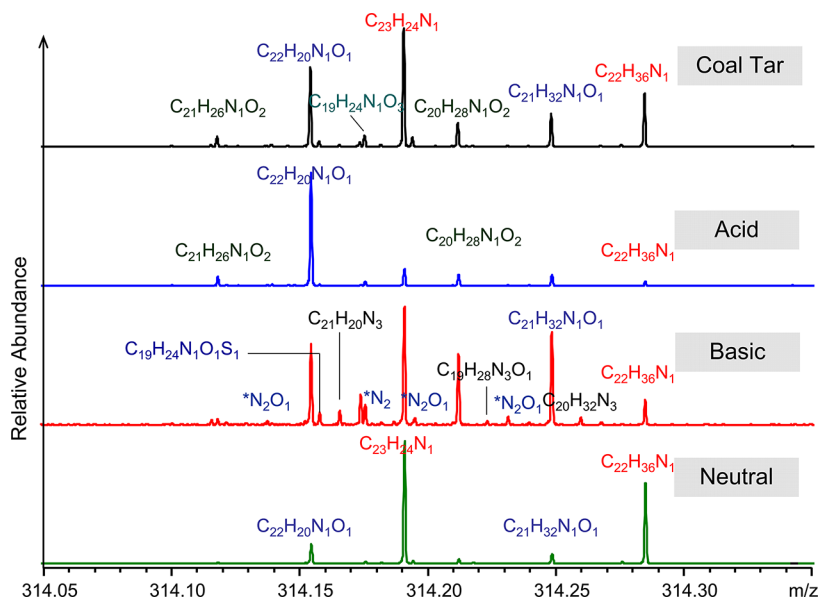


Figure 6. Mass-scale-expanded positive-ion ESI FT-ICR MS spectra of MTCT and its subfractions at m/z 314.

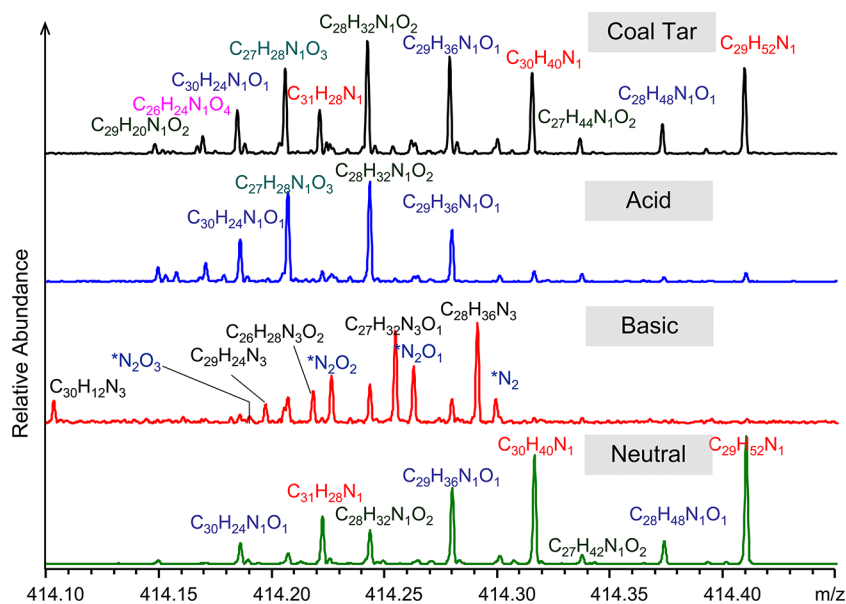


Figure 7. Mass-scale-expanded positive-ion ESI FT-ICR MS spectra of MTCT and its subfractions at m/z 414.

should be the same as the MTCT, because the basic nitrogen compounds were enriched in the BF and only the basic nitrogen compounds (except for sulfoxides, which are found in fossil fuels) can be ionized. Nevertheless, the FT-ICR MS results showed that the basic nitrogen compounds were not only enriched in the BF but were also found in the NF as well as the AF. Even though the ESI FT-ICR MS analysis is not quantitative, the results showed that the relative composition and distribution of basic nitrogen compounds were much more complex than expected.

Figure 5 showed that the basic nitrogen compounds in the BF had relatively low molecular weights. Large-molecular-weight basic nitrogen compounds were more refractory to the acidic/basic extraction. A similar phenomenon has been observed in extracting large naphthenic acid molecules.³² It is likely that large molecules have a weaker effective acidic or basic functionality than the small molecules.

Figures 6 and 7 show the detailed molecular compositions of MTCT and its subfractions. Unexpectedly, the AF responded strongly to the positive-ion ESI. Most of the peaks in the AF indicated that the nitrogen compounds also contained oxygen. This suggested that all of the detected compounds have basic nitrogen groups with oxygen atoms, which are likely to have a phenol or carboxyl group, which makes the basic nitrogen compounds exhibit acidic property and report to the AF. Non-oxygen-containing nitrogen compounds were also present in the AF, indicating that the AF was not “truly acidic”. The non-oxygen-containing nitrogen compounds carried into the AF were likely due to its molecular polarity, which enhanced their solubility in the aqueous phase. Compounds with multi-heteroatoms were preferentially extracted from the oil phase into the AF and BF.

A total of 14 class species were assigned to the nitrogen compounds in the MTCT and its subfractions, as shown in

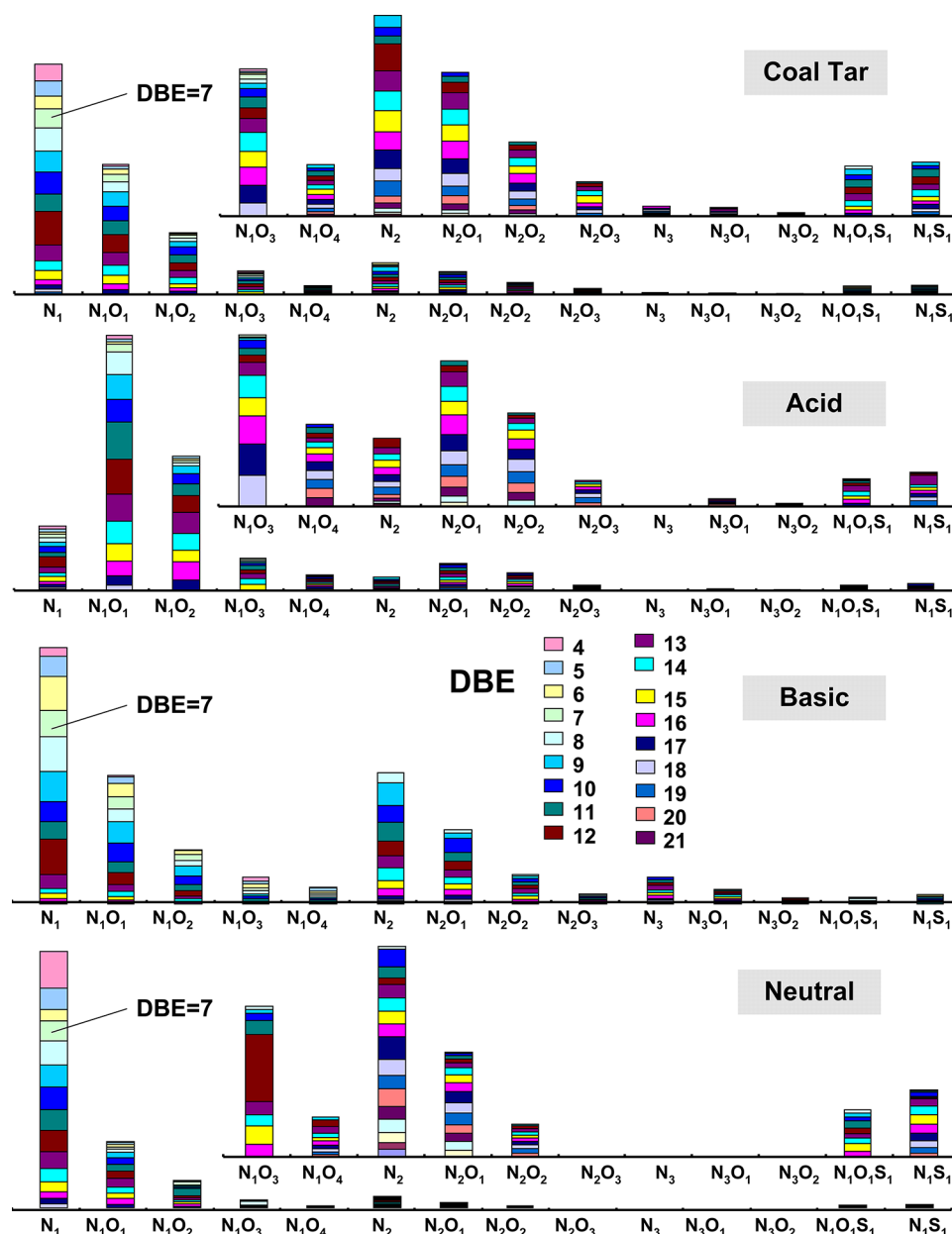


Figure 8. Relative abundance of basic nitrogen class species in MTCT and its subfractions derived from the mass spectra of Figure 5.

Figure 8. All assigned molecules contain at least one nitrogen atom; a clear indication of only the basic nitrogen functional groups responded strongly to the ionization in the positive-ion ESI analysis. The N_1 class species was dominant in the MTCT, followed by N_1O_1 and N_1O_2 class species. Oxygen-containing nitrogen compounds were enriched in the AF. Compounds with 2–3 nitrogen atoms were enriched in the BF. The NF had a relatively high abundance of mono-nitrogen compounds.

Figure 9 shows the isoabundance plots of the double-bond equivalence (DBE) versus carbon number of selected class species in the MTCT and its subfractions. Figure 9 shows that N_1 , N_1O_1 , and N_2 class species were present in the MTCT and its fractions, N_3 class species was present in the MTCT and BF, and N_1O_2 and N_2O_1 class species were present in the BF. The distribution pattern of N_1 class species in the MTCT was distinctly different from that in the coking-derived gas oils (CGOs)^{28,33}. The CGOs also have abundant basic nitrogen compounds with a normal distribution of DBE as a function of

the carbon number. The MTCT had abundant N_1 compounds with 12 DBE, which corresponded to the structure of azapyrenes. The minimum carbon number of 15 also confirmed this deduction. In addition, these class species exhibited high abundance in GC–MS chromatograms [total ion current (TIC) and m/z 203] shown in Figure 4.

Molecules with high DBE values and low carbon numbers likely exhibit strong basic functionality but were selectively enriched in the AF. In view of the sequence of acidic/basic extraction steps, in which the AF was obtained prior to the BF, the enrichment of basic nitrogen compounds is likely due to their high polarity, which cause them to be more soluble in water. If the BF was obtained before the AF, the nitrogen compounds with high DBE values and low carbon numbers would likely enrich in the BF and the yield of BF would be much higher. Attempts were made to reverse the sequence of obtaining the BF prior to the AF. However, severe water/oil emulsification occurred in the alkaline solution system, which prevented the phase separation.

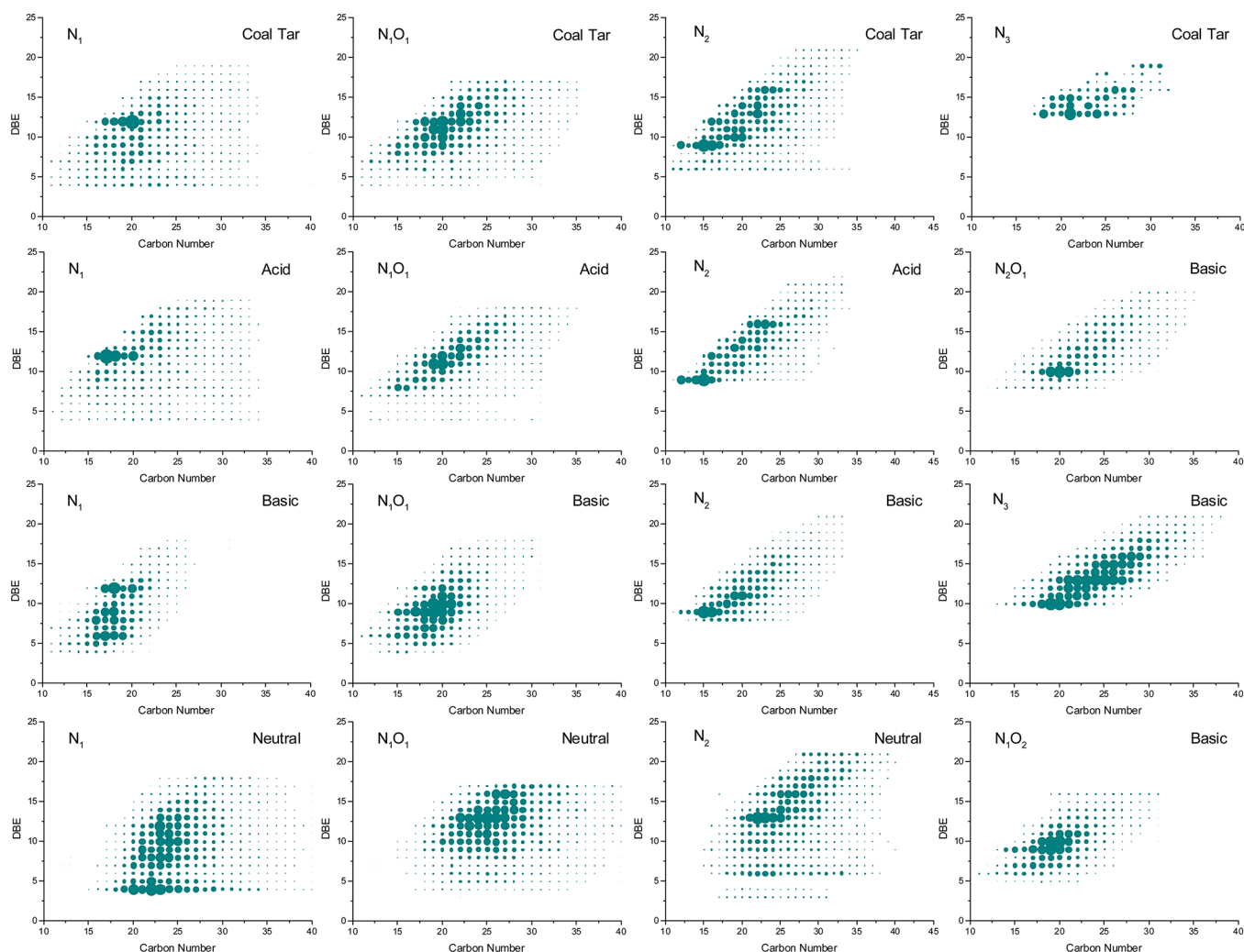


Figure 9. Isoabundance plots of DBE versus carbon number of various class species in the MTCT and its subfractions.

4. CONCLUSION

The dominant compounds in MTCT were aromatics, phenols, and normal alkanes. The number of carbon atoms in the substituent chains varied over a relatively broad range for each homology. The composition of narrow distillate fractions varied: light naphtha (<100 °C) had a high benzene content, which is an unsuitable gasoline blending stock; middle distillates (160–240 °C) enriched with phenols, which is a good extraction feedstock for chemical products; and heavy distillates (>240 °C) are a hydrotreating feedstock for clean fuel production. The MTCT had large amounts of acidic and basic components, consisting of oxygen- and nitrogen-containing molecules. The BF accounted for 2.68 wt % MTCT. Most of the oxygen-containing molecules exhibited a weak acidity and were partially extracted into the AF. Basic nitrogen compounds co-existed in the acidic, basic, and neutral fractions of MTCT. However, the molecular compositions of basic nitrogen compounds were different among these fractions: molecules with low carbon numbers and high aromaticities were found in the AF and BF, whereas mono-nitrogen basic compounds were abundant in the NF.

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Notes

The authors declare no competing financial interest.

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