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GC/MS ANALYSIS OF COAL TAR COMPOSITION PRODUCED FROM COAL PYROLYSIS

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ABSTRACT. Coal tar is a significant product generated from coal pyrolysis. A detailed analytical study on its composition and chemical structure will be of great advantage to its further processing and utilization. Using a combined method of planigraphy-gas chromatograph/mass spectroscopy (GC/MS), this work presents a composition analysis on the coal tar generated in the experiment. The analysis gives a satisfactory result, which offers a referable theoretical foundation for the further processing and utilization of coal tar.

KEY WORDS: Coking-coals, Coal pyrolysis, Coal tar, GC/MS

INTRODUCTION

Coal pyrolysis is one of the significant approaches for the comprehensive utilization of coal, one important product of which is coal tar. Coal tar can be utilized as raw materials for various industries such as synthetic fiber, dyestuff, medication, coating and national defense. It is also a type of raw materials from which phenols, naphthalenes and anthracene can be extracted for the production of washing oil, cementitious agents, antiseptic agents, and catalytic hydrogenated to produce gasoline, diesel oil, etc. Therefore, a detailed analytical study on the composition and chemical structure of coal tar will be advantageous to its processing and utilization, and enable it to be a chemical and power fuel materials of great value.

Because of the complex characteristics of coal tar, most previous researches have used some form of pre-separation, dividing a mixture into several fractions to provide further identification and quantitative analysis for it. There have already been some reports on the analytical methods of coal tar. These methods mainly involved UV-fluorescence spectroscopy (UV-F) [1, 2], size exclusion chromatography (SEC) [2], nuclear magnetic resonance method (NMR) [3-5], gas chromatography [6-8], high performance liquid chromatography [9, 10], gas chromatography-Fourier transform infrared spectrometry [11, 12], and gas chromatography-mass spectrometry (GC/MS) [13-16]. It is believed that using GC/MS can carry out most effectively a thorough analysis of the complex composition of coal tar.

In this study, an experimental research on coal pyrolysis was conducted in a fixed-bed cracking furnace, with coking-coals as the feeding material. A detailed composition analysis was carried out on the coal tar generated in the experiment through a combined method of planigraphy-GC/MS; therefore a satisfactory analytical result obtained, which offers a referable theoretical foundation for the further processing and utilization of coal tar.

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EXPERIMENTAL

Materials

The materials used for this study were the coking-coals from the Coking-Plant of Wuhan Iron and Steel (Group) Corp. and their main patria are Handan, Yihan, and Xiaotunjie, which are in the middle of China. The physicochemical data of the coking-coals are given in Table 1.

Table 1. Categories and chemical characteristics of the coking-coals.

Coal categories		Proximate analysis		Total sulfur	Colloid layer thickness		caking index
		Aad (%)	Vdaf (%)	St (%)	Y (mm)	X (mm)	Gr.1 (%)
Coking-coals	Handan	10.41-11.19	21.20-24.39	0.92-1.30	20-25	19-21	73-78
	Yihan	7.28-9.21	23.47-25.25	0.45-0.55	12-15	27-28	78-81
	Xiaotunjie	10.08-11.88	23.11-25.16	0.66-0.72	20-30	19-20	80-83

(Handan, Yihan, Xiaotunjie are just the local names of the patria of coking-coals used in this study.)

Equipments and process

The schematic diagram of coking-coals pyrolysis **is** shown in Figure 1. The coking-coals were heated up to 1100 °C in the cracking furnace on the fixed bed, cracked at the high temperature and followed by evolving of coal gas. The generated coal gas, after dust removal by a cyclone cleaner, entered into the tar condensers. The tar component in the coal gas was then collected by condensation. After dust removal and tar separation, the coal gas entered into the next waste water separation and gas purification process.

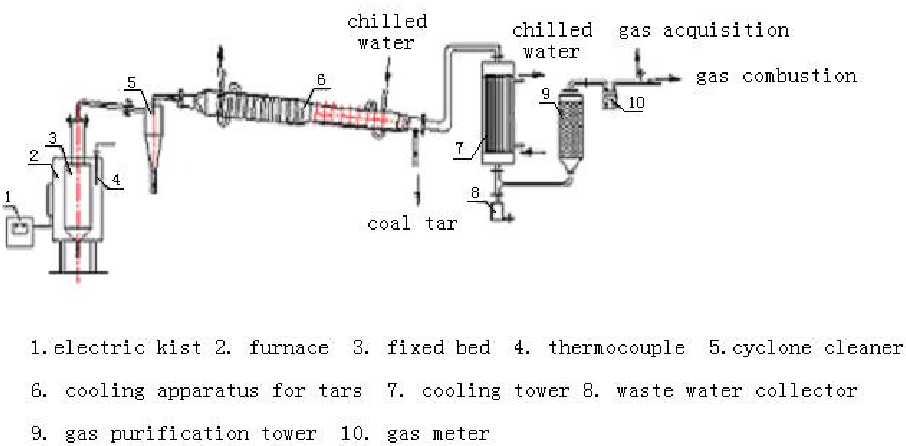

Figure 1. Flow-sheet of equipment of coal pyrolysis and products separation.

Analytical methods

Sample planigraphy pre-treatment

By means of planigraphy pretreatment, the coal tar sample collected from coking-coal pyrolysis was separated into several groups with different polarities, which facilitate the GC/MS analysis. The planigraphy, taking the solid adsorbent as the stationary phase, is the liquid-solid chromatography, carrying out separation inside the column tube.

Silica gel and alumina were used as the adsorbent materials in this experiment. They have been activated at 105 °C and at 400 °C for 4 h, respectively and 2 g activated alumina and 3 g activated silica gel were loaded into the planigraphy column successively each time. The schematic diagram of planigraphy column is shown in Figure 2.

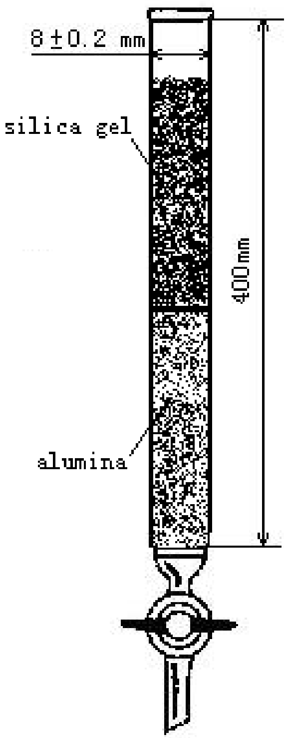

Figure 2. Schematic diagram of planigraphy column.

Using the difference of adsorbability between various types of organics in tar and adsorbents and the difference of polarity between various eluents, a successive separation of the coal tar sample into aliphatics, aromatics, ester, and polar was achieved by eluting with normal pentane, benzene, ethyl acetate and methanol, respectively. Each effluent was collected after 5 times successive elution of the corresponding eluent with the volume of 5 mL each time. The remainder of the coal tar sample was regarded as asphaltene group. The collected effluents were concentrated by using nitrogen gas to evaporate the eluent, and then they were further analyzed using a GC/MS analysis to determine their components.

During the planigraphy pretreatment, the relative weight of each group (aliphatics, aromatics, ester and polar) of coal tar was weighed using an analytical balance (precision: 0.0001 g). By subtracting the weight of former 4 groups from the total quantity of coal tar, the asphalt portion was then obtained. The relative weight percentage of each group in total is therefore calculated.

GC/MS analysis of the tar composition

Normally, asphaltene is a mixture of various polymers with very heavy molecular weights, and can hardly be separated and analyzed through ordinary GC methods. Therefore, in this study the GC/MS analysis has been carried out only on aliphatics, aromatics, ester and polar generated from the planigraphy pretreatment of tar. The composition of asphaltene will be investigated using other analytical methods in the future work.

A gas chromatography (GC, Varian 3900) and a mass spectrometer (MS, Saturn 2100T) were used in this study. The basic parameters are given below.

GC condition. A VF-5ms 30 m x 0.25mm (ID) x 0.25μm quartz capillary column was used, helium served as the carrier gas, injector temperature was 280 °C, split ratio 15:1.0, and sample size 1.0 μL. The GC temperature programming is given in Table 2.

Table 2. Temperature programming of composition analysis on different groups in coal tar.

Item	Injector temperature (°C)	Initial temperature (°C)	Hold time (min)	Rate (°C /min)	Final temperature (°C)	Hold time (min)
Aliphatics	280	70	3	5	280	15
Aromatics	280	70	3	6	280	15
Ester	280	60	3	5	280	15
Polar	260	60	3	5	260	20

MS condition. The ionization mode was EI, electron bombarding energy was 70 eV, charging multiplier tube voltage at 500 V, scan range form m/z 40 to 650 at 3 scan/s was used, solvent delay at 3 min.

Comparing with the MS self-contained chromatogram library, the species of every group were identified, and the relative proportion of each species (%) was obtained by dividing the individual peak area with the total peaks areas.

RESULTS AND DISCUSSION

The weight percentage of every tar group (aliphatics, aromatics, ester and polar) is given in Table 3.

Table 3. Percentage of every tar group in coal tar.

Group	Aliphatics	Aromatics	Ester	Polar	Asphaltene
Percentage (%)	18.12	34.15	5.95	5.48	36.30

Figures 3-6 show the typical gaschromatograms of aliphatics, aromatics, ester and polar group in the coal tar, respectively. According to the **GC**, combined with MS analysis, the qualitative and semi-quantities analyses of each peak appearing in the gaschromatogram can be determined. The components of analytical results of various groups are given in Tables 4-7, respectively.

The aliphatic compounds in coal tar (Table 4) mainly involve various C_6-C_{28} paraffin hydrocarbons, alkene, and a small amount of alicyclic compounds. Moreover, there are about 2% materials that cannot be identified, which shows the complication of their chemical nature. Among the aliphatic group of the coal tar, the proportion of alkene is larger than alkane. The reason may be that alkane components trend to form alkene during the dehydrogenation process under the high temperature condition of pyrolysis [17].

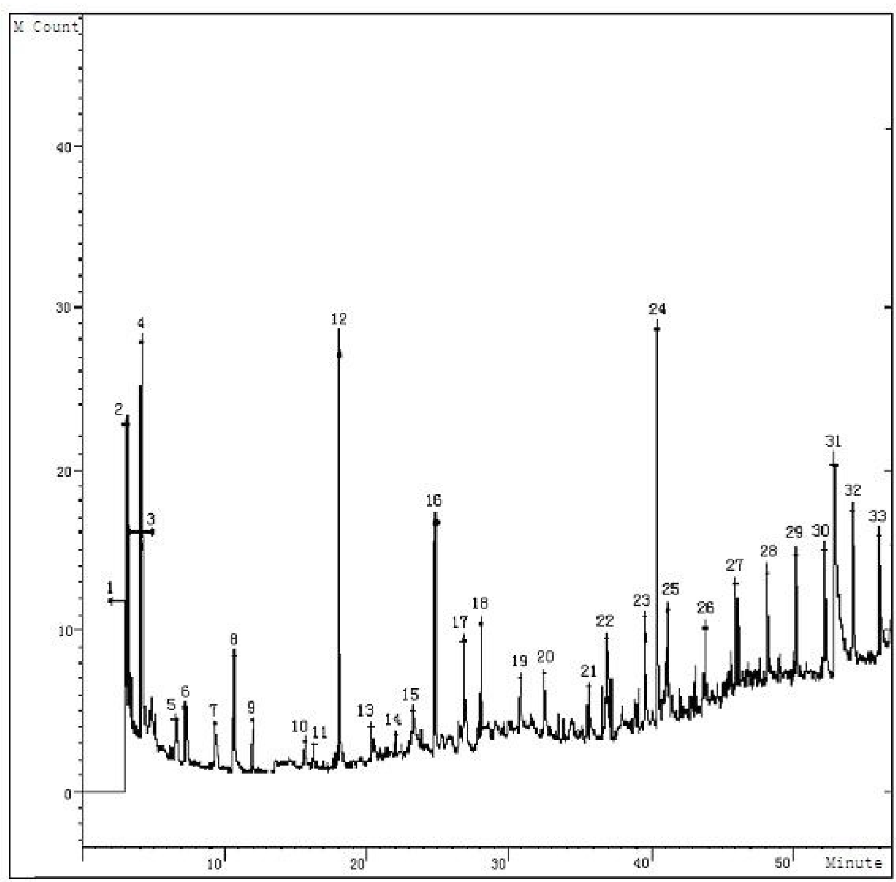

Figure 3. Typical gaschromatogram of aliphatics group in the coal tar.

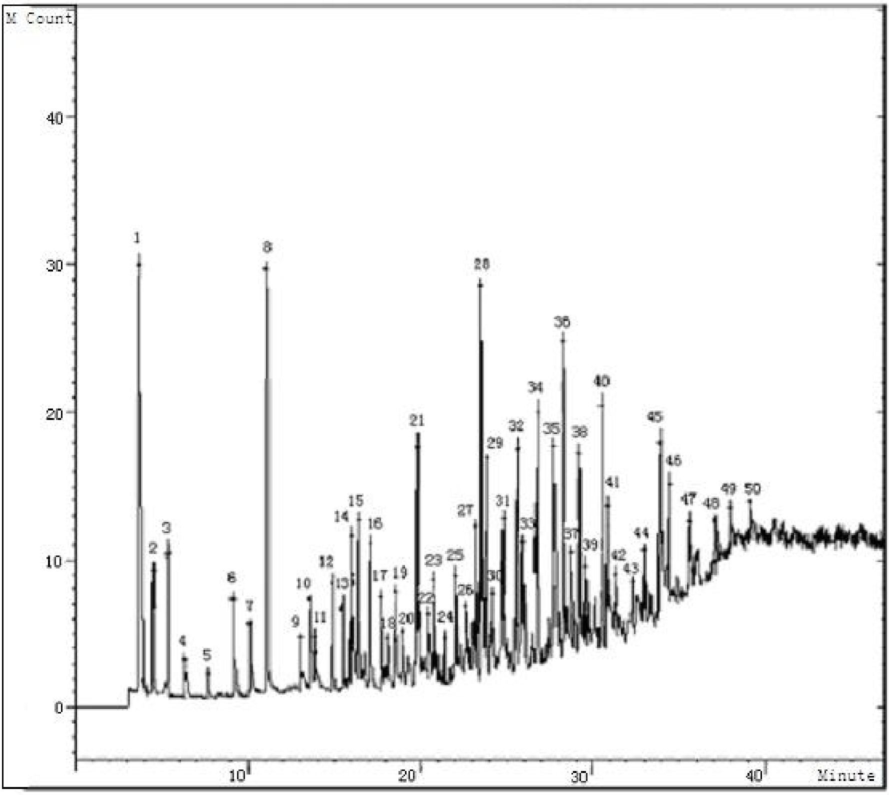

Figure 4. Typical gaschromatogram of aromatics group in the coal tar.

Main components of aromatics group (Table 5) can be divided into monoaromatics, polycyclic aromatics hydrocarbons (PAHs), and some heterocycle materials (PANH, PASH) containing N and S, etc. No benzene was found in the coal tar samples, according to coal tar definition - the mixture of compounds whose molecular weight was above that of benzene. In addition, benzene was as an eluant in the pretreatment as such it was excluded from the aromatics group. The amount of toluene in aromatics group of the coal tar was about 10.64%, which was in accordance with other study claiming that there is comparatively more toluene in the aromatics group [18]. PAHs mainly consist of naphthalene, indene, biphenyl, phenanthrene, anthracene, pyrene, etc. and their derivatives, with their maximum molecular weight reaching above 200. The total amount of naphthalene and its derivatives was the largest in the PAHs of the coal tar; the proportion of naphthalene accounts for above 10%. If α-methylnaphthalene, ethylnaphthalene, dimethylnaphthalene and trimethylnaphthalene, etc. will be included the proportion will be even higher. PANH mainly includes pyridine, quinoline, indole, and some derivatives. PASH is mainly some derivatives of thiophene.

The ester groups of coal tar (Table 6) contain mainly some oxygen compounds, such as ketone, acid, furan, as well as some small amount of aromatics compound containing N and S, such as benzene sulfonic acid and nitrile, etc.

The main components of polar groups in the coal tar (Table 7) are various phenols, methylphenols, dimethylphenols, naphthols and their derivatives, which account for a large proportion. In addition, some heterocyclic compounds containing N and S are also found at certain proportion, together with a few ketone, isoquinoline, carbazole and acridine.

The overall species detected and their contents in coal tar are summarized in Table 8, from which some conclusions can be made as follows. Totally 129 compounds in coal tar were determined using GC/MS analytical method. Among them there are 33 types of aliphatic hydrocarbons that account for 17.33% of the coal tar, and 37 types of aromatics hydrocarbon compounds, which accounts for 27.41%, such as phenylmethane, *p*-xylene, naphthalene and their derivatives. There are 10 kinds of naphthalene products that accounts for 10.74% of the coal tar contents, which is correspondent with the previous result of the 10% contents of naphthalene in high temperature coal tar. Totally 13 kinds of phenols compounds and 12 kinds of acid ester compounds are also determined. Moreover, 22 kinds of alkaline constituents are found with small amount contents in the coal tar, which are mainly derivatives of pyridine, quinoline and nitrile.

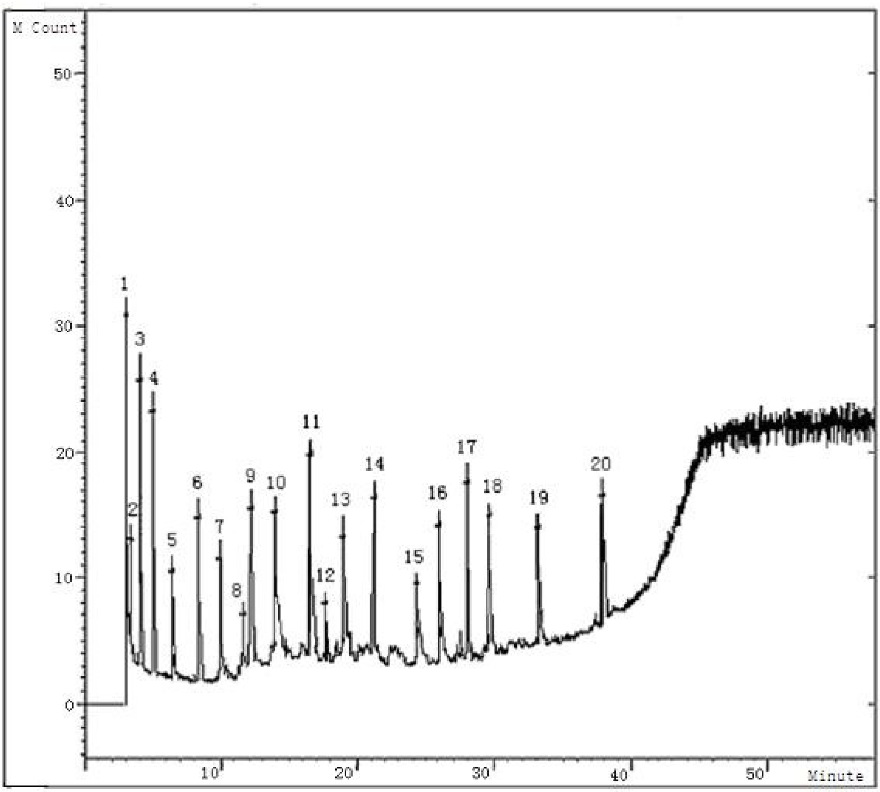

Figure 5. Typical gaschromatogram of ester group in the coal tar.

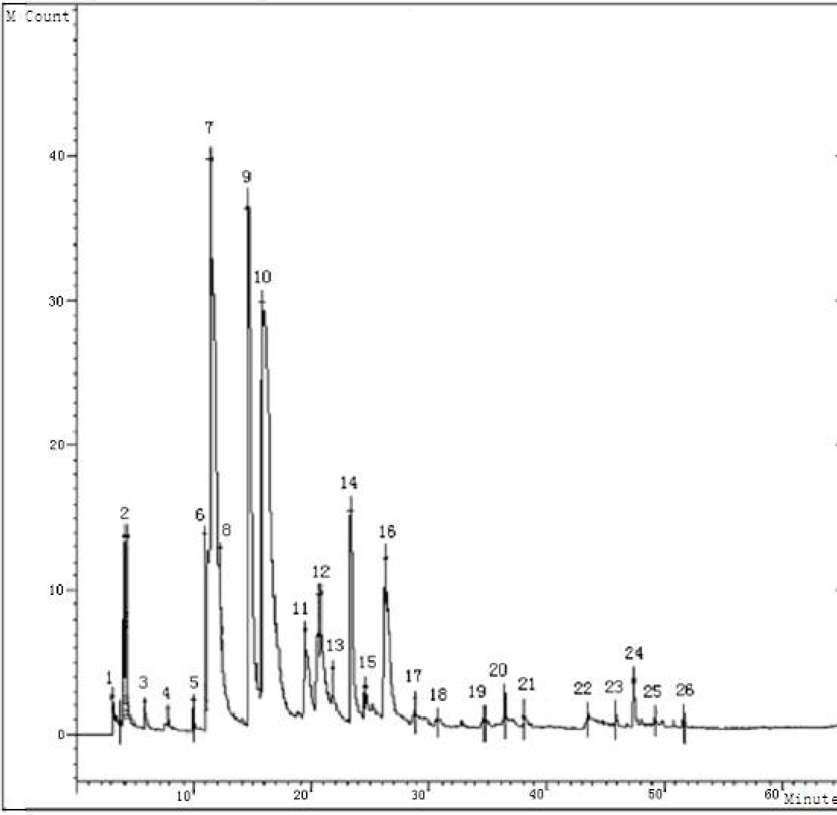

Figure 6. Typical gaschromatogram of polar group in the coal tar.

Table 4. Compositions analysis results of aliphatics group in the coal tar.

Peak number	Hold time	Compound name	Relative percent [a]	Percentage in coal tar
1	3.173	Butane,2,2-dimethyl	3.18	0.576
2	3.368	1-Pentene,2,4,4-trimethyl	3.26	0.592
3	3.642	Hexanaphthene	2.15	0.389
4	4.063	1,3,5-Cycloheptatriene	12.65	2.293
5	6.454	3,4-Heptene	1.02	0.185
6	7.132	1,3,5,7-Cyclooctatetraene	2.36	0.428
7	8.675	Dicyclooctane,1,3,5-triene	4.14	0.750
8	10.735	1-Heptene	1.96	0.355
9	11.882	2-Hexene,3-ethyl	1.12	0.204
10	15.627	Octane	1.72	0.312
11	17.328	Octane,2-methyl	0.86	0.157
12	19.034	Octane,4-ethyl	9.81	1.778
13	20.652	1-Octene	0.68	0.123
14	23.012	1-Nonene,3-methyl	0.24	0.043
15	24.325	Undecane	3.21	0.582

16	25.432	Undecane,2,6-dimethyl	4.67	0.846
17	27.324	Decane,3-methyl	3.31	0.599
18	28.643	Undecane,2,3-dimethyl	3.26	0.591
19	29.193	1-Undecene,4-methyl	1.32	0.239
20	31.241	Dodecane	2.53	0.458
21	32.614	1,12-Tridecdiene	0.37	0.067
22	34.647	1-Tridecene	1.67	0.302
23	37.215	Tridecane	2.83	0.513
24	39.463	1- Tetradecene	1.31	0.237
25	40.862	1- Pentadecene	11.32	2.050
26	41.237	Eicosane,7-hexyl	1.41	0.255
27	43.617	Phenanthrene,9-dodecylte tradecahydro	1.53	0.278
28	46.287	Heptadecane,9-hexyl	2.57	0.467
29	48.625	Octadecane,3-ethyl-5-(2-ethyl butyl)	1.36	0.246
30	51.631	Nonadecane	1.18	0.213
31	53.827	17-Pentacosene	1.23	0.223
32	54.351	Nonadecane,3-methyl-5-(2-ethyl butyl)	2.07	0.375
33	56.436	Docosane,7-hexyl	6.34	1.149
		Total identified	98.64	17.875
		Total unknown	1.36	0.246

[a]The proportion of the relative contents (%) of each peak (component) with total peaks area.

Table 5. Compositions analysis results of aromatics group in the coal tar.

Peak number	Hold time	Compound name	Relative percent	Percentage in coal tar
1	3.57	Phenylmethane	10.64	3.636
2	4.439	*p*-Xylene	1.98	0.676
3	5.421	Pyridine	1.52	0.519
4	6.524	Xylene	1.62	0.553
5	7.726	Indene	0.68	0.232
6	9.237	Quinoline	1.76	0.601
7	10.416	Indene,methyl	1.53	0.523
8	11.042	Naphthalene	13.06	4.464
9	13.263	Naphthalene,2-methyl	2.03	0.694
10	13.812	Naphthalene,1-methyl	3.96	1.354
11	14.124	Indole	0.34	0.116
12	15.225	Biphenyl	0.91	0.311
13	15.763	Indole,1-methyl	0.69	0.236
14	16.235	Naphthalene,2,6-dimethyl	2.13	0.728
15	16.548	Naphthalene,1,4-dimethyl	2.58	0.882
16	17.058	Biphenylene	2.37	0.810
17	17.749	1-Isopropenyl naphthalene	1.62	0.534
18	18.575	Dibenzo furan	0.23	0.079
19	18.729	Naphthalene,1,6,7-trimethyl	1.65	0.564
20	19.809	Fluorene	0.34	0.116
21	20.334	1,1-Biphenyl,4-methyl	2.17	0.742
22	20.816	6H-Dibenzo[b,d]-pyran	0.12	0.041
23	21.657	11-Heneicosanone	0.43	0.147
24	22.094	9H-Fluorene,2-methyl	0.07	0.024
25	22. 737	BenzylBenzoate	1.27	0.434
26	23.201	4-Phenanthrenol,1,2,3,4-tetrahydro-4-methyl	0.78	0.267
27	23.564	Phenanthrene	1.51	0.516
28	24.581	Phenol,4-(2-phenyl ethenyl)	10.62	3.629

29	24.697	Phenyl-pyridin	1.34	0.458
30	25.052	Benzo[b]quinoline	0.13	0.044
31	25.514	Benzenamine,4,4-methylenebis	1.29	0.441
32	25.910	Anthracene,2-methyl	3.97	1.357
33	26.243	9H-Fluorene-2-carbonitrile	0.14	0.048
34	26.783	Naphthalene,2-phenyl	2.43	0.831
35	27.524	Phenanthrene,1,7-dimethyl	2.04	0.697
36	28.027	9,10-Dimethy anthracene	5.37	1.835
37	28.275	Pyrene	0.47	0.161
38	29.147	Fluoranthrene	2.47	0.844
39	29.45	Pyrene,1-methyl	0.41	0.140
40	30.637	Benzo[kl]xanthrene	3.34	1.142
41	30.819	7H-Benzo[c]fluorene	0.94	0.321
42	32.267	Pyrene,1,3-dimethyl	0.21	0.072
43	33.037	Benzo[b]naphtha[2,1-d]thiophene	0.03	0.010
44	33.364	Benzo[a]phenazine,12-oxide	0.26	0.089
45	33.957	Triphenylene	2.25	0.769
46	34.437	Naphthacene	1.56	0.533
47	34.619	Benzo[c]phenanthrene,5-methyl	0.39	0.133
48	36.316	Benzo[a]pyrene	0.35	0.119
49	38.121	Benzo[k]fluoranthrene	0.34	0.116
50	39.285	Benzo[ghi]perylene	0.25	0.085
		Total identified	98.59	33.673
		Total unknown	1.41	0.481

Table 6. Compositions analysis results of ester group in the coal tar.

Peak number	Hold time	Compound name	Relative percent	Percentage in coal tar
1	3.113	*o*-Acetyl-L-serine	9.67	0.575
2	3.309	1-Deoxy-d-mannitol	4.72	0.281
3	3.982	2-Cyclopentanone	9.54	0.568
4	5.023	2,5-Dimethyl furan	9.12	0.543
5	6.627	2-Furanketon	6.16	0.367
6	8.482	2-Methylpropyl acetate	6.39	0.380
7	10.021	Carbamicacid,phenylester	5.83	0.347
8	11.624	Propionic acid 2-methylbenzyl ester	1.34	0.079
9	12.232	Cyclohexane-3-nitrile	5.37	0.319
10	14.617	Phenol,2,3-dimethyl	3.87	0.230
11	16.725	3,4-Dimethyl benzyl alcohol	8.28	0.493
12	17.618	Methyl-nitro carbonate acid ethyl ester	1.03	0.061
13	18.664	4-Hydroxy benzene sulfonic acid	2.32	0.138
14	21.276	Butylated Hydroxytoluene	4.64	0.276
15	24.527	dl-5-Methyltryptophan	2.03	0.121
16	24.612	Dibenzofuran	3.14	0.187
17	26.827	Acridine	4.68	0.278
18	27.994	1,2-Benzedicarboxylicacid, bis(2-methylpropyl)ester	3.39	0.202
19	29.617	Dibutylphthalate	3.17	0.189
20	37.904	1,2-Benzenedicarboxylicacid,disooctyl ester	3.52	0.209
		Total identified	98.21	5.843
		Total unknown	1.79	0.107

Table 7. Compositions analysis results of polar group in the coal tar.

Peak No.	Hold time	Compound name	Relative percent	Percentage in coal tar
1	3.173	Cyclopentanone	3.67	0.201
2	4.064	Cyclopentanone,2-methyl	5.58	0.306
3	4.119	Pyridine,2-methyl	0.18	0.009
4	5.762	Pyridine,3-methyl	0.21	0.012
5	7.834	Pyridine,2,6-dimethyl	0.31	0.017
6	11.021	Aniline	1.14	0.062
7	12.195	Phenol	27.36	1.499
8	12.825	1,2-benzyl diol	0.92	0.050
9	14.635	Phenol,2-methyl	13.36	0.732
10	15.820	Phenol,3-methyl	17.81	0.976
11	20.660	Phenol,3,5-dimethyl	2.76	0.151
12	21.194	Phenol,1,2-dimethyl	5.67	0.311
13	22.172	Phenol,3,4-dimethyl	0.71	0.039
14	23.235	Isoquinoline	5.58	0.306
15	25.192	Indole,2-methyl	0.68	0.037
16	26.568	phenol,1,2-diphene,4-ethyl	5.12	0.281
17	29.193	Quinoline,7-methyl	1.48	0.081
18	30.749	1H-Indole,2-methyl	0.37	0.020
19	34.667	Propanenitrile,3,3-thiobis	0.67	0.037
20	36.452	2-Naphthalenol	0.93	0.052
21	38.002	Diethyl Phthalate	0.34	0.019
22	43.581	Isoquinoline,2-oxide	0.39	0.021
23	45.929	Acridine	0.26	0.014
24	47.403	Carbazole	1.72	0.094
25	49.693	3,4-Biphenyldicarbonitrile	0.48	0.027
26	51.726	3,4-Phenanthroline	0.57	0.031
		Total identified	98.27	5.385
		Total unknown	1.73	0.095

Table 8. Categories of various components and contents in the coal tar.

Categories	Compositions	Kinds count	Content (%)
Aliphatics	Paraffin hydrocarbons	19	9.988
	Alkene	14	7.341
Aromatics	Benzene and its derivatives	7	7.997
	Naphthalene and its derivatives	10	10.738
	Phenanthrene, anthracene and their derivatives	11	6.963
	Indene and its derivatives	2	0.755
	Fluorene and its derivatives	3	0.461
	Pyrene and its derivatives	4	0.492
Oxygenic compounds	Alcohols	2	0.774
	Phenols	13	8.493
	Aldehyde, ketone	5	1.589
	Acid, ester	12	2.754
	Furan and its derivatives	3	0.809
	Pyran and its derivatives	1	0.041
Nitrogenous compounds	Priding and its derivatives	5	1.015
	Indole and its derivatives	4	0.409
	Quinoline and its derivatives	5	1.053
	Aniline and its derivatives	2	0.503

	Nitrile and its derivatives	4	0.431
	Phenazine and its derivatives	1	0.089
	Carbazole and its derivatives	1	0.094
Sulfuric compounds	Thiophene and its derivatives	1	0.010
Unknown		9	0.929
Total		138	63.728

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