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Composition of phenolic compounds in wastewater from the fixed-bed gasification of Baishihu coal

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Abstract Crude phenols extracted using organic solvent from the wastewater of a typical fixed-bed gasification process was used as a raw material, and the distillation range was analyzed. The wide and narrow fractions of the raw material derived from distillation range analysis were cut using a real boiling point distillation device. The phenolic compounds in the different fractions were then qualitatively and quantitatively analyzed by gas chromatography after derivatization pretreatment. The yield of the < 290 °C fraction was 68.50% (mass fraction). A total of 33 effective phenolic compounds were identified in this fraction, and the percentage of identified phenols was nearly 80%. The contents of eight phenolic compounds were high, with phenol being the most abundant (26.34%) followed by catechol (13.44%). The contents of the remaining six abundant phenols ranged from 4% to 8%. The sum of the contents of m-cresol and p-cresol exceeded 12%, and the content of 5-indenol was nearly 8%. The yield of the fraction rich in low-grade phenols (< 230 °C) was 35.40%. The content of phenol in this fraction was more than 40%, the total content of cresol was over 23%, and the total content of m-cresol and p-cresol was nearly 20%. At room temperature, the 235–245 °C and 245–260 °C fractions were white crystals in which the catechol content was approximately 50%, and the 5-indenol content was more than 10%. The contents of these two high-value-added phenolic compounds are low in typical coal tar, making them difficult to extract. However, due to their strong polarity and good water solubility, catechol and 5-indenol are enriched in gasification wastewater by water selection, allowing their further extraction.

Keywords Gasification wastewater · Phenolic compounds · Derivatization pretreatment · Gas chromatography

1 Introduction

China leads the world in coal production and total coal consumption. In 2019, China's total coal consumption exceeded 4 billion tons (Dai et al. 2017), accounting for over half of global total consumption. Since the release of the 13th Five-Year Plan, China has made significant progress in coal-to-liquid, coal-to-natural gas, and coal-to-olefin technologies. The 14th Five-Year Plan represented a key stage in the development of the modern coal chemical industry, which is taking the lead in clean, efficient, green, and low-carbon development.

Coal gasification is an important part of the modern coal chemical industry. The primary goal of coal gasification wastewater treatment is zero discharge or near-zero discharge. In the future, high-value-added products will ideally be extracted simultaneously with the zero-discharge treatment of gasification wastewater containing phenols, polycyclic aromatic hydrocarbons, and benzene derivatives (Wang et al. 2018). At present, the recovery of phenol and ammonia during gasification wastewater treatment generally includes three processes: deacidification, extraction dephenolization, and deamination (Qin et al. 2015; Qian et al. 2016). The phenol and ammonia recovery process

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applied direct affects the quality of the resulting effluent and the recycling efficiency (Ji et al. 2016; Yu et al. 2010). Common extractants used in the recovery process include benzene, heavy benzene, heavy solvent oil, methyl isobutyl ketone, and isopropyl ether. These extractants have a higher partition coefficient for low-boiling phenols and polyphenols. Phenol and its homologues, particularly binary phenols such as catechol, are important intermediates in the chemical industry and are widely used in many fields such as medicine, plastics, dyes, and synthetic fibers (Li et al. 1998; Xue et al. 1998; Liu et al. 2012; Zhao et al. 2017). Understanding the characteristics of phenolic compounds in gasification wastewater would facilitate the identification of appropriate separation methods and lead to the extraction of phenolic compounds with high economic value added. This effort is in line with China's national plan and could further broaden the comprehensive utilization of coal gasification byproducts.

In general, the total phenol content in wastewater from fixed-bed gasification is 5000–20,000 mg/L. Although the phenol content is not high, the phenol composition in coal gasification wastewater is quite different from that in coal tar. Due to the polarity-based separation by water and extractant, phenolic compounds with strong polarity are enriched in coal gasification wastewater, while the types of miscellaneous such as ethyl phenol, propyl phenol and xylenol and the content of neutral oil are greatly reduced compared to in coal tar (Ge and Jin 1995; Wang et al. 2011; Zhao 2016). This situation provides an opportunity for the extraction of phenolic compounds with high value added. At present, researchers primarily use gas chromatography–mass spectrometry to qualitatively analyze phenolic compounds. However, it is difficult to achieve good separation with direct chromatography because phenolic compounds have strong polarity, low volatility, and a large number of isomers. In this study, the composition and characteristics of phenolic compounds extracted from gasification wastewater were analyzed. First, the extract was divided into several fractions to achieve further enrichment. The enriched phenolic components were then pretreated by silica ether derivatization to improve the separation of the phenolic compounds. Finally, the compositions of the phenolic compounds in the different fractions were studied in detail by gas chromatography. The findings provide valuable guidance for the future extraction and efficient utilization of phenolic compounds in gasification wastewater.

2 Experiment

2.1 Experimental materials

The raw material used in the experiment was the crude phenol product obtained from the wastewater of a typical fixed-bed gasification process (a ketone extraction process in a phenol and ammonia recovery unit in Xinjiang, China). The properties of the crude phenol raw material were quite different from those of traditional coal tar; the gasification wastewater contained more water-soluble polar substances and fewer neutral oils than the coal tar.

2.2 Experimental and analytical methods

To analyze the composition of phenolic compounds in the raw material and locate the most phenolic compounds range, the distillation range of the raw material was analyzed. The sample weight was approximately 250 g, and the test was carried out using a 500-mL simple distillation unit according to ASTM D 1860.

According to the distillation range analysis results, the product cutting scheme was designed. According to ASTM D 2892, approximately 3 kg of raw material was weighed, and the target fractions were cut from the sample with a 5-L real boiling point precision distillation device.

Although each fraction was enriched, the fractions still contained many monomeric phenolic compounds. Thus, if the sample was analyzed directly by chromatography, a considerable number of monomeric phenols would not be effectively separated. Further, because the sample contained many isomers, the chromatogram would have double peaks or overlapping peaks, preventing accurate qualitative and quantitative analysis. To comprehensively and efficiently analyze the monomeric phenols, derivatization was adopted as a pretreatment method in this study with the following steps. First, 15–25 μL of silicon etherification reagent was added to a sample weighing approximately 0.8–1.0 mg (Mao et al. 2009). The sample was then diluted with dichloromethane and placed in a 25-mL volumetric flask for 8–12 h at room temperature. If a single sample produced multiple peaks in the subsequent chromatographic determination, the pretreatment reaction was not sufficient, and it was necessary to increase the amount of silylation reagent or extend the mixing time.

The samples were analyzed qualitatively and quantitatively by gas chromatography based on the external standard method. The gas chromatograph (Agilent model 6890 g) was equipped with a flame ionization detector and a DB-Petro column (100 m × 0.25 mm × 0.25 μm). The injection port temperature was 280 °C, and the detector temperature was 300 °C. The heating program was as

follows: hold at 80 °C for 5 min; increase to 200 °C at 4 °C/min; hold at 200 °C for 3 min; and increase to 250 °C at 2 °C/min. Each sample was measured at least twice, and the relative deviation was controlled within 2%.

3 Results and discussion

3.1 Distillation range of the raw material

The basic properties of the raw material were analyzed (Table 1). To enrich the main phenolic compounds in the raw material, the distillation range of the raw material was analyzed. The sample weight was 238.2 g. Under vacuum distillation, the final distillation point reached 300 °C at atmospheric pressure. The results of the distillation range analysis are shown in Table 2 and Fig. 1.

The < 300 °C fraction accounted for approximately 70% (volume fraction) of the crude phenol raw material. This fraction was further distilled, producing a heavier (yellow in color and higher in viscosity) distillate than the < 300 °C fraction. After distillation, the > 300 °C fraction was poured out while it was hot and solidified upon cooling, similar to tar pitch. Table 1 and Fig. 1 show that the < 300 °C fraction was mainly concentrated in two distillation sections corresponding to temperature ranges of 180–210 °C and 245–270 °C. According to the analysis of the monomer properties, the raw material contained no obvious xylenol fraction, and the mass fraction of 210–230 °C fraction was less. The distillation scheme was designed to effectively enrich the main phenolic compounds and avoid interference from other phenols. A 6-L real boiling point distillation device was used for the cutting test of the narrow fraction. The test results are shown in Table 3 and Fig. 2.

Eight fractions were obtained by cutting the narrow fraction. In all narrow fractions, the mass fractions of the phenol-rich (< 188 °C), o-cresol-rich (188–198 °C), and binary phenol-rich (245–260 °C) fractions were greater than 10%. The mass fraction of the m-cresol-rich (198–208 °C) fraction was greater than 6%. In the range of 208–235 °C, the contents of the two xylenol-rich fractions were less than 3%. Phenolic compounds rich in hydroxyl groups and with strong polarity were enriched in the wastewater.

To analyze the total contents of low-level phenols and effective phenols, the raw material was enriched and cut at < 230 °C and < 290 °C, respectively (Table 4).

After cutting the wide fraction, phenol, cresol, and xylenol were mainly enriched in the < 230 °C fraction, and they accounted for a total mass fraction of 35.40%. In addition to the enrichment of low-grade phenols, the < 290 °C fraction also contained effective phenols such as

Table 1 Properties of the raw material

Analysis item	Data
Element analysis (mt%) (Mass fraction)	
C	72.29
H	7.86
N	0.45
S	0.15
O	19.25
Density at 24 °C (g/mL)	1.085
Water content (mt%)(Mass fraction)	0.05

Table 2 Distillation range analysis results of the raw material

Volume (mL)	Temperature (°C)	Cumulative yield (V%) (Volume fraction)
Initial boiling point (IBP)	174	–
5	188	2.2
10	191	4.4
15	192	6.6
20	194	8.8
25	195	11.0
30	199	13.2
35	200	15.4
40	203	17.6
45	203	19.8
50	205	22.0
55	207	24.2
60	209	26.4
70	218	30.2
75	230	32.4
80	232	34.6
85	245	36.8
90	246	39.0
95	253	41.2
100	255	43.4
105	256	45.6
110	257	47.8
115	259	50.0
120	260	52.5
125	265	54.7
130	268	56.9
135	274	58.1
140	275	60.3
145	277	62.5
150	279	64.7
155	281	66.9
160	286	69.1

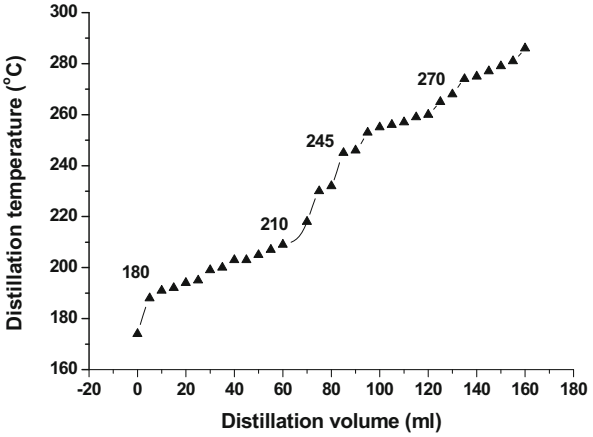


Fig. 1 Distillation temperature vs. distillation volume of the raw material

Table 3 Fractions obtained from the narrow boiling cuts of the raw material

Fraction number	Distillation range (°C)	Yield (wt%)
1#	< 188	15.60
2#	188–198	10.15
3#	198–208	6.32
4#	208–218	2.45
5#	218–235	2.05
6#	235–245	3.96
7#	245–260	13.95
8#	> 260	45.52

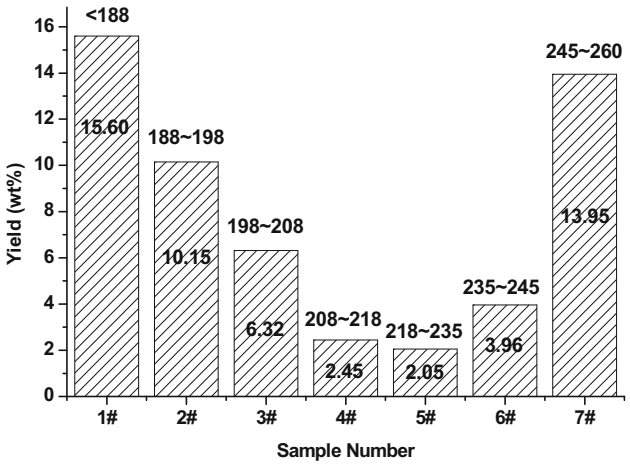


Fig. 2 Narrow fraction analysis results of the raw material

trimethylphenol, ethyl phenol, propyl phenol, binary phenol, and indenol, accounting for a mass fraction of 68.50%. In subsequent experiments, monomeric phenols were analyzed in these two broad fractions.

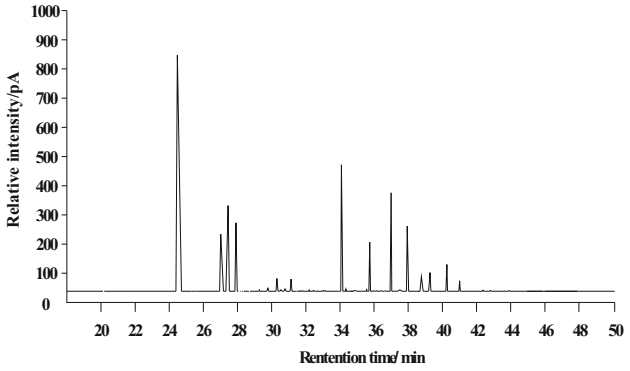


Fig. 3 Gas chromatogram of the < 290 °C fraction

Table 4 Fractions obtained from the wide boiling cuts of the raw material

Fraction number	Distillate range (°C)	Yield (wt%)
9#	< 230	35.40
10#	< 290	68.50

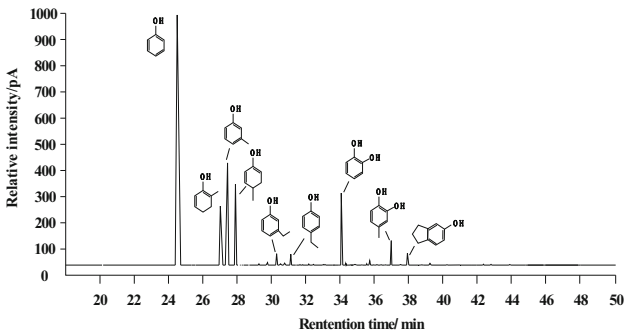


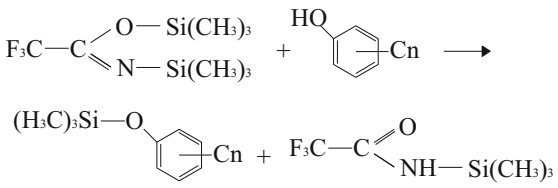
Fig. 4 Gas chromatogram of the < 230 °C fraction

3.2 Analysis of monomeric phenols

Although the raw material was cut into different fractions, each fraction still contained a large amount of monomeric phenols. The boiling points of these monomers and particularly the isomers were similar, making it difficult to accurately quantify them by column chromatography. To improve the separation of the monomeric phenols, the sample was first pretreated. After silica etherification and derivatization, the corresponding ethers were generated and analyzed by capillary column gas chromatography, demonstrating a good separation effect. The phenols easily reacted with the silylation reagent BTSFA to form siloxane at room temperature (Shi 2012). The reaction equation can be expressed as follows:

Table 5 Quantitative analysis of phenolic compounds in the < 290 °C fraction

No.	Compound	Content in the < 290 °C fraction (wt%)	Content in the crude phenol raw material (wt%)	No.	Compound	Content in the < 290 °C fraction (wt%)	Content in the crude phenol raw material (wt%)
1	Phenol	26.43	18.10	18	3-Propyl phenol	0.02	0.01
2	o-Cresol	3.89	2.66	19	Pyrocatechol	13.44	9.21
3	m-Cresol	6.52	4.47	20	2.3.5-Trimethylphenol	0.05	0.03
4	p-Cresol	5.82	3.99	21	2.3.6-Trimethylphenol	0.08	0.05
5	o-Ethylphenol	0.31	0.21	22	3.4.5-Trimethylphenol	0.01	0.01
6	2.5-Xylenol	0.27	0.18	23	Resorcinol	3.39	2.32
7	m-Ethylphenol	1.04	0.71	24	4-Methylcatechol	7.89	5.40
8	3.5-Xylenol	–	–	25	Hydroquinone	0.59	0.40
9	2.4-Xylenol	0.36	0.25	26	5-Indanol	4.65	3.18
10	p-Ethylphenol	0.93	0.64	27	5.6.7.8-Tetrahydro-1-naphthol	0.34	0.23
11	2-Isopropyl phenol	–	–	28	5.6.7.8-Tetrahydro-2-naphthol	0.11	0.08
12	2.6-Xylenol	0.25	0.17	29	1-Naphthol	0.07	0.05
13	2.3-Xylenol	0.57	0.39	30	2-Naphthol	0.17	0.12
14	3.4-Xylenol	0.51	0.35	31	2-Phenylphenol	0.03	0.02
15	3-Isopropyl phenol	0.02	0.01	32	3-Phenylphenol	0.05	0.03
16	2-Propyl phenol	0.10	0.07	33	4-Phenylphenol	0.03	0.02
17	4-Isopropyl phenol	0.04	0.03	34	Total	77.98	53.42



First, the < 290 °C fraction was analyzed by chromatography to detect the composition of effective phenols in the raw material.

As shown in Fig. 3 and Table 4, 33 effective monomers were identified, and the total amount of identified phenols was nearly 80%. Eight monomeric phenols had high contents in this fraction, with phenol being the most abundant (26.43%) followed by catechol (13.44%). These two monomers had strong polarity and were enriched in the gasification wastewater. The contents of the remaining six major monomers ranged from 4% to 8%. The content of 5-indenol was nearly 8%, and the sum of the contents of m-cresol and p-cresol exceeded 12%. The differences in the boiling points of these phenolic compounds are above 10 °C; thus, these compounds could be the main products for extraction and purification.

According to the boiling point data of the main phenolic compounds, the compositions of phenolic compounds in the < 230 °C, 235–245 °C, and 245–260 °C fractions were analyzed.

As shown in Fig. 4, phenol and cresol were the main components in the < 230 °C fraction. The content of xylenol in gasification wastewater was low because of its two methyl groups and poor hydrophilicity. The contents of the six xylenol isomers were less than 1%. These characteristics are quite different from those of typical coal tar.

Table 6 lists the nine monomeric phenolic compounds with contents exceeding 1% in the < 230 °C fraction. The total amount of identified phenols was greater than 85%. The content of phenol was more than 40%, the total content of cresol was more than 23%, and the total content of m-cresol and p-cresol was nearly 20%. Due to the limited fractionation effect, some high-boiling-point monomers were detected in this fraction; the contents of catechol, 4-methyl-catechol, and 5-indenol were 9.04%, 3.90%, and 2.51%, respectively. The contents of these high-value-added phenolic compounds are typically low in coal tar, making their extraction difficult. However, due to their strong polarity and good water solubility, those compounds are enriched in gasification wastewater after water selection, providing an opportunity for their further extraction.

The 235–245 °C fraction only accounted for approximately 4% of the raw material. However, due to its enrichment in phenolic compounds, this fraction was a white crystal at room temperature. As shown in Fig. 5 and Table 7, this fraction contained nine primary compounds, and the total amount of identified phenols was nearly 90%.

Table 6 Quantitative analysis of main phenolic compounds in the < 230 °C fraction

No.	Compound	Content in the < 230 °C fraction (wt%)	Content in the crude phenol raw material (wt%)	No.	Compound	Content in the < 290 °C fraction (wt%)	Content in the crude phenol raw material (wt%)
1	Phenol	40.03	14.17	6	p-Ethylphenol	1.11	0.39
2	o-Cresol	5.87	2.08	7	Pyrocatechol	9.04	3.20
3	m-Cresol	9.23	3.27	8	4-Methylcatechol	3.90	1.38
4	p-Cresol	8.24	2.92	9	5-Indanol	2.51	0.89
5	m-Ethylphenol	1.27	0.45	10	Total	81.20	28.75

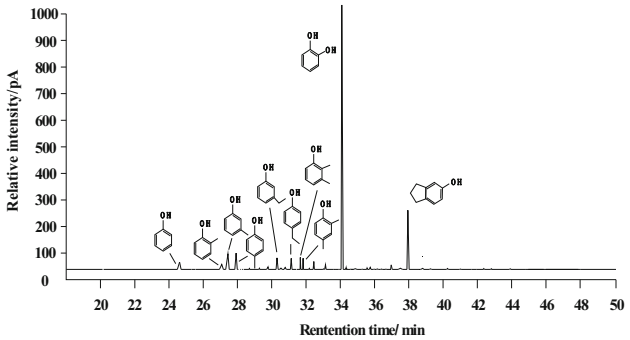


Fig. 5 Gas chromatogram of the 235–245 °C fraction

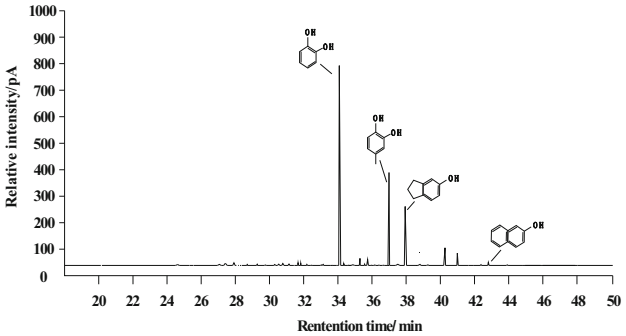


Fig. 6 Gas chromatogram of the 245–260 °C fraction

Among the nine compounds, catechol was the most abundant (57.34%) followed by 5-indenol (11.54%).

The 245–260 °C fraction was also a white crystal at room temperature. As shown in Fig. 6 and Table 8, this fraction contained three main compounds, and the total amount of identifiable phenols was nearly 90%. Among the phenolic compounds, catechol was the most abundant (46.10%) followed by 4-methyl-catechol (27.80%), while 5-indenol had the lowest content (15.48%).

4 Conclusions

The crude phenols extracted from typical gasification wastewater were mainly concentrated in two fractions: 180–210 °C and 245–270 °C. In all the narrow fractions, the mass fractions of the phenol-rich (< 188 °C), o-cresol-rich (188–198 °C), and binary phenol-rich (245–260 °C) fractions were more than 10%, while that of the 198–208 °C fraction rich in m-cresol exceeded 6%. In the

Table 7 Quantitative analysis of main phenolic compounds in the 235–245 °C fraction

No.	Compound	Content in the < 235–245 °C fraction (wt%)	Content in the crude phenol raw material (wt%)	No.	Compound	Content in the < 235–245 °C fraction (wt%)	Content in the crude phenol raw material (wt%)
1	m-Cresol	2.87	0.11	6	3.4-Xylenol	2.87	0.11
2	p-Cresol	2.90	0.11	7	Pyrocatechol	57.34	2.27
3	m-Ethylphenol	3.13	0.12	8	4-Methylcatechol	2.85	0.11
4	p-Ethylphenol	2.31	0.09	9	5-Indanol	11.54	0.46
5	2.3-Xylenol	3.33	0.13	10	Total	89.14	3.53

Table 8 Quantitative analysis of main phenolic compounds in the 245–260 °C fraction

No.	Compound	Content in the < 245–260 °C fraction (wt%)	Content in the crude phenol raw material (wt%)	No.	Compound	Content in the < 245–260 °C fraction (wt%)	Content in the crude phenol raw material (wt%)
1	Pyrocatechol	46.10	6.43	3	5-Indanol	15.48	2.16
2	4-Methylcatechol	27.80	3.88	4	Total	89.38	12.47

208–235 °C fraction, the contents of the two xylenol-rich fractions were less than 3%. Phenolic compounds with abundant hydroxyl groups and strong polarity were enriched in the gasification wastewater.

Thirty-three effective monomers were identified in the < 290 °C fraction, and the total amount of identified phenols was nearly 80%. Among the eight monomers with the highest contents, phenol was most abundant (26.43%) followed by catechol (13.44%). The contents of the remaining six major monomers ranged from 4% to 8%. The content of 5-indenol was nearly 8%, and the sum of the m-cresol and p-cresol contents was more than 12%. The differences in the boiling points of these phenolic compounds are above 10 °C; thus, these could be the main products for extraction and purification.

The content of phenol in the < 230 °C fraction was more than 40%, the total content of cresol was more than 23%, and the total content of m-cresol and p-cresol was nearly 20%. This fraction could be used as the intermediate product for extracting low-grade phenol. At room temperature, the 235–245 °C and 245–260 °C fractions were white crystals in which the catechol content was approximately 50%, and the 5-indenol content was more than 10%. The contents of these two high-value-added phenolic compounds are low in typical coal tar, making them difficult to extract. However, due to their strong polarity and good water solubility, catechol and 5-indenol are enriched in gasification wastewater after water selection, providing an opportunity for their further extraction.

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Declarations

Conflict of interest We claim that none of the material in the paper has been published or is under consideration for publication elsewhere and there is no conflict of interest with others.

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