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Analysis of coal tar derived from pyrolysis at different atmospheres

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ABSTRACT

Compared with traditional pyrolysis processes, the integrated process of CO_2 reforming methane and coal pyrolysis (CRMP) can obviously improve the tar yield. However, the structural information and formation mechanism of coal tar in the integrated process are still unknown. To compare the chemical composition of coal tars under different atmospheres, GC and GC/MS were used to analyze the volatile fractions of tar obtained by pyrolysis of Shendong coal at 750 °C in CRMP process and to be compared with those under nitrogen, hydrogen, methane, carbon dioxide atmospheres. The results show that phenol and its alkyl-substituted homologs from C_1 to C_3 are the major products of the volatile fractions (distillate below 300 °C). ^{1}H NMR and ^{13}C NMR analyses of coal tars show that the tar derived from CRMP process is mainly composed of alkyl-substituent attached to aromatic ring. The mechanism analysis of CRMP process indicated that the increase in tar yield of CRMP process should be attributed to the free radical reaction.

1. Introduction

Pyrolysis is considered as an effective way for clean use of coal because desulfurized char and tar can be obtained [1–4]. Moreover, high added-value chemicals, especially aromatic compounds, can be separated from tar, so it is significant to obtain high tar yield in coal pyrolysis. In our previous studies [5,6], a novel integrated process of CO_2 reforming methane and coal pyrolysis (CRMP) was developed. Compared with traditional pyrolysis under inert gases or hydrogen atmosphere, CRMP process can obviously improve the tar yield. Furthermore, carbon dioxide and methane, as the greenhouse gases, are commercially cheaper than hydrogen as the traditional improving tar yield atmosphere. However, it is still unknown as to the composition and formation mechanism of tar in CRMP process.

GC and GC/MS analyses are effective methods to analyze the compositions of coal tar volatile fractions. GC/MS analysis provides data at a molecular level, in which mass spectrum gives the structural information of compounds separated by gas chromatogram. It was reported that tars derived from coal processing technologies such as liquefaction, pyrolysis and extraction were investigated by this technology [7–11]. Such studies can provide information of composition of tars and formation process of the tar compounds. One of the disadvantages of GC/MS analysis is that the compounds with a boiling point higher than 300 °C is hard to be volatilized and detected, and those with a lower boiling point than solvent may be overlaid by solvent peak in chromatograms. ^{1}H NMR and ^{13}C NMR analyses can provide the proton and carbon distributions of compounds, respectively, and have received many researchers' attention [8,12–17]. For the complex mixture such as coal tar, NMR cannot give information of accurate compositions. However, it can provide structural information of the high boiling temperature compounds that GC/MS analysis cannot be detected. Therefore, to explore compositions and structure of the tar derived from CRMP process, in this work, the tar from CRMP of Shendong (SD) coal was analyzed by GC, GC/MS, ^{1}H NMR and ^{13}C NMR, and compared with those from pyrolysis under N_2, H_2, CH_4 and CO_2 atmospheres.

To better compare and validate spectra results of tars as well as the formation mechanism of coal tar compounds in CRMP process, coal char, as an another important product in coal pyrolysis process, was also investigated by FT-IR analysis, which can provide information of functional groups. Additionally, according to the GC/MS analyses of tar, phenolic hydroxyl as the main functional group in coal, was measured by titrimetric method.

Thus, the main object of this work is to get composition and structural information of tars generated from coal pyrolysis at different atmospheres and CRMP process by GC and GC/MS analysis. And we also try to understand the formation mechanism of coal tar compounds in CRMP process through qualitative and quantitative ^{1}H NMR and ^{13}C NMR analysis.

2. Experimental

2.1. Sample and pyrolysis experiment

Shendong coal used in the experiment was crushed to the particle size of below 100 mesh. The proximate and ultimate analyses of coal sample are shown in Table 1.

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Table 1
Proximate and ultimate analyses of coal sample.

Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
M_{ad}	A_d	V_{daf}	C	H	N	S	O[a]
9.80	4.50	33.72	79.53	4.16	0.91	0.48	14.92

[a] By difference.

The low-temperature tar was obtained by pyrolysis on a vertical fixed-bed reactor under different atmospheres [5]. During the experiment, about 5 g coal sample was placed in a stainless-steel tube reactor with 18 mm i.d. and 150 mm in length. The reactor was heated from room temperature up to final pyrolysis temperature of 750 °C in 5 min, and kept it at 750 °C for 25 min in different atmospheres. The flow rate of gas was 500 ml/min for N_2, H_2, CH_4, CO_2 atmosphere. In CRMP process, the gas flow rate was 400 ml/min CH_4 and 400 ml/min CO_2. About 1 g catalyst (13%Ni/γ-Al_2O_3, prepared by incipient wetness impregnation method) was placed above the coal bed, and thus the gas mixture of CH_4 and CO_2 flows to the catalyst layer before entering into the coal bed. Coal tar from pyrolysis experiment was condensed by cool trap at a temperature of −15 °C to separate liquid and gas.

2.2. GC and GC/MS analysis of tar

Owing to the analysis limitation of GC, the compounds with a boiling point higher than 300 °C cannot be detected and should be separated. Detailed separation process is as follows: the coal tar was dissolved in dichloromethane and the water in tar was absorbed by Na_2SO_4. The solution was filtrated to remove Na_2SO_4 and then distilled at 300 °C to meet the GC demand. Distillate including CH_2Cl_2 was kept in chromatogram bottle for analysis.

GC analysis of tar was carried out using an Agilent 6890N gas chromatograph equipped with a HP-5 capillary column and a flame ionization detector (FID), and helium as carrier gas with a flow rate of 1.2 ml/min. The detector and injector temperatures were 280 °C and the column temperature was started at 60 °C for 5 min, then heated to 280 °C at a heating rate of 4 °C/min and holding 10 min at 280 °C. The compounds were identified by GC/MS using an Agilent 6890N gas chromatograph coupled with Agilent 5975 mass detector. The operation condition of GC was similar to those used in the GC analysis (DB-5 capillary column) and the mass spectrum condition is as follows: solvent delay, 6 min; interface temperature, 250 °C; electron impact ion source temperature, 230 °C; quadruple spectrometer temperature, 150 °C; and scan from 50 to 300.

2.3. NMR spectra analysis of tar

^{1}H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were obtained with a Varian Inova 400 spectrometer at an operating temperature of 25 °C using $CDCl_3$ as solvent. The sample was prepared by dissolving the tar in $CDCl_3$ and CS_2, using TMS as an internal reference. The concentration used was about 0.1 g/ml for ^{1}H NMR and 0.8 g/ml for ^{13}C NMR. Different from that of GC/MS analysis, the sample analyzed in NMR spectra is the total coal tar dissolved in CS_2 and $CDCl_3$.

2.4. FT-IR analysis of coal and char

The FT-IR spectra of the raw coal and coal char were measured by an EQUINOX55 spectrometer using KBr pellet technique. The Shendong coal and char were kept in an oven at 110 °C for 10 h to remove external water. The ratio of coal or char to KBr was about 1:160. The spectra were recorded from 4000 to 400 cm^{-1} at 2 cm^{-1} resolution.

2.5. Quantitative measurement of phenolic hydroxyl in coal and char

Total acid and carboxyl in coal and char were measured by titrimetric method based on the following reactions:

$$Ba(OH)_2 + 2HA \rightarrow BaA_2\downarrow + 2H_2O\ \text{(total acid)}$$
$$2(\text{—COOH}) + Ca(CH_3COO)_2 \rightarrow \text{—COO—Ca—OOC—} + 2CH_3COOH$$
$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O\ \text{(carboxyl)}$$

Phenolic hydroxyl was obtained by subtraction of total acid and carboxyl.

3. Results and discussion

3.1. Tar yield of coal pyrolysis under different atmospheres

Tar yields of coal pyrolysis at 750 °C under different atmospheres are listed in Table 2. It can be seen that Shendong coal has a higher tar yield under hydrogen than that under nitrogen atmosphere, and methane alone behaves as inert gas; CO_2 has a promotion to tar yield. Moreover, CRMP process can obviously enhance the tar yield to 32.0%, which is 3.2 and 2.6 times as that under N_2 and H_2 atmosphere, respectively. Similar results have been obtained in our previous works [1,5,6] and literatures [18,19].

3.2. Composition of tar volatile fractions determined by GC and GC/MS analysis

The amount of volatile fractions (distillate below 300 °C) of tar obtained from coal pyrolysis under different atmospheres is different and the results are shown in Table 3. It can be seen that the percentage of distillate for coal tar under N_2, H_2 and CO_2 atmospheres is about 70% to total tar, and that from CRMP process is 83.3%, much higher than those from other atmospheres. This indicates that the CRMP process not only enhance the tar yield but also improve the quality of coal tar.

The chromatograms of Shendong coal tars generated under different atmospheres are presented in Fig. 1. The figures show that the tars generated from different atmospheres and CRMP process have similar chromatograms under the same GC conditions. Phenol and its alkyl-substituted homologs from C_1 to C_3 are the major products in the volatile fractions of the tars, here C_1, C_2 or C_3 represents the total number of carbon substituted to the aromatic ring. Other minor aromatic compounds such as naphthalene and its alkyl-substituted homologs, anthracene, xanthene, phenanthrene and dibenzofuran were also identified. Only an extremely small amount of *n*-alkane and *n*-alkene were found.

Phenolic compounds are represented by four pieces according to the number of alkyl-substituted carbon. For cresol, P1, three isomers are represented by two peaks because the *m*- and *p*-cresol can not be separated in the chromatographic conditions used in this work. P2 represents the C_2 alkyl-substituted phenols including

Table 2
Tar yield of coal pyrolysis at 750 °C under different atmospheres.

Atmosphere	N_2	H_2	CH_4	CO_2	CRMP
Tar yield (wt.%, daf)	10.0	12.3	10.2	15.3	32.0

Table 3
Amount of distillate at 300 °C of coal tar generated under different atmospheres.

Atmosphere	N_2	H_2	CH_4	CO_2	CRMP
Distillate (%)	66.3	72.6	52.2	68.1	83.3