Research article

Behaviors of coking and radicals during reaction of volatiles generated from fixed-bed pyrolysis of a lignite and a subbituminous coal

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ABSTRACT

The reaction of volatiles generated from coal during pyrolysis determines the yield and quality of products. To understand this reaction in detail particularly on the condensation reaction that forms coke, this paper studies the reaction of volatiles generated from a lignite and a subbituminous coal using a two-stage fix-bed reactor, with the first stage for coal pyrolysis and the second stage for reaction of volatiles. The yields of tar, gas and coke formed on the wall and presented in tar at a second-stage temperature range of 440–700 °C and a residence time range of 1.5–6.9 s are quantified. The concentration, g value and linewidth of radicals in tars, mainly in coke presented in tars, are measured by electron spin resonance (ESR) and discussed to explore the transformation of coke in structure. It is found that the reactions of volatiles generated from the lignite and the subbituminous coal are different in the temperature range studied but the structure of coke formed in these two volatiles differs mainly at temperatures lower than 600 °C. The proportion of coke formed on the reactor wall is small at 440 °C, but large at 650 and 700 °C, close to 50% in 4.2 s. The increase in concentration and decreases in g value and linewidth of radicals with increasing temperature over time suggest that the coke undergoes condensation, leading to loss in oxygen and increase in aromaticity.

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1. Introduction

Coal pyrolysis is a direct way to produce tar and has been widely studied in the past. Except for the slow pyrolysis technique in the coking industry, most of the fast coal pyrolysis techniques aiming at tar yields higher than that of the coking are not satisfactory. The main problem found in the fast pyrolysis techniques was the poor dust/volatiles separation, which led to a high dust content of tars as well as frequent clogging of the volatile product lines and downstream devices [1]. In addition, the yields of dust-free and processable light oil are low. Extensive efforts in increasing pyrolysis heating rate to reduce pyrolysis time failed to solve these problems, because they increased temperature gradient between the coal and the heating sources which inevitably accelerated the pyrolysis reaction of volatiles produced, leading to the formation of more gas and more heavy fractions, such as pitch and coke [2,3].

It is well recognized that coal pyrolysis follows a two-step radical mechanism: the generation of volatile radical fragments from the solid coal and the reaction of the volatile radical fragments in the gas phase as well as on the coal surface. The former step is also called by some the primary reaction, while the latter step the secondary reaction.

Many studies suggested that overreaction of volatile fragments is responsible for low tar yield and high coke formation [3–5]. Liu et al. analyzed the temperature increases of volatiles upon their generation from coal in various types of pyrolysis reactors and correlated the temperature increases with the yield and composition of tar. They showed that the extent of volatiles' reaction varies greatly with reactor type and operating conditions, mainly due to the difference in temperature-time profile the volatiles have experienced [3,6]. In particular, they reported that the volatiles' temperature increase and reaction time are approximately 40 °C and 6 s, respectively, in a slow heating moving bed Lurgi–Spuelgas (L-S) reactor, while 200–300 °C and 2 s in a fast heating fluidized-bed reactor or in a reactor using a solid heat carrier. The slow heating reactor results in a higher tar yield than the fast heating reactors [3].

Doolan et al. [7], Katheklakis et al. [8], Hayashi et al. [9,10] and Zieliński et al. [11] studied the volatiles' reaction in fluidized-bed reactors. They reported that an increase in temperature or in reaction time decreased the tar's yield and H/C ratio, and increased the tar's heavy component content. Katheklakis et al. [8] noted that the loss of tar via volatiles' reaction was significant at temperatures as low as 500 °C. In a range of 580–750 °C, the amount of tar loss due to extended reaction time, approximately 9.35–26.02% from 0.8 to 4.5 s, was similar to that due to a temperature increase of approximately 70 °C. Serio et al. [12] and Xu and Tomita [4] studied the volatiles' reaction in two-stage fixed-bed reactors, where the second stage was for the volatiles'

reaction, and reported similar results as those found in fluidized-bed reactors.

Besides the in-situ studies discussed above, the volatiles' reaction was also studied ex-situ by heating the tars collected from coal pyrolysis to high temperatures. Hesp and Waters [13] investigated the reactions of two tars collected from a vertical-retort and a fluidized-bed reactor, and reported that in the reaction time of 1–440 s the oil yield decreased with an increase in temperature. The main reaction products were hydrocarbon gases in 500–700 °C while coke and H_2 in 800–1000 °C. He et al. [14] studied the reaction of tars collected from pyrolysis of various coals in a fixed-bed reactor. They found that the conversion of tars to coke (the matter insoluble in tetrahydrofuran (THF)) was significant at temperatures of 500 °C or higher. The coke formation in 2 s was 10% of tar at 500 °C and 40% at 700 °C based on the second-order coking kinetics they developed for a reaction time range of 4 h. Wu et al. [15] reported that the coking of a bituminous coal tar was notable at temperatures higher than 420 °C and completed in 10 min at temperatures higher than 480 °C. They also showed that the coking could be expressed by the zero-order or zero-order plus autocatalytic kinetics with activation energies of 128–138 kJ/mol for a reaction time range of 0–10 min.

It is also recognized that the reaction of volatiles produced in coal pyrolysis also follows a radical mechanism. However, only a few studies can be found in the literature on the radicals' reaction, which may be attributed to the fact that the response time of electron spin resonance (ESR) available for radical measurement is much longer than the reaction time of most of the free radicals. Therefore, the free radicals which are active in the reaction cannot be detected by ESR. The radicals detected by ESR are mainly the stable ones which are structurally confined in large molecules such as pitch and coke [16]. For instance, Kim et al. [17] showed that the radical concentration of volatiles produced in coal pyrolysis increased in a few minutes at 510 °C, which resulted in coking on the reactor wall. He and Wu et al. showed that the reaction of tars collected in coal pyrolysis increased their radical concentration at temperatures as low as 350 °C, and the increases in radical concentration and in quantity of THF insoluble matters were closely related [14, 15].

It is noted that the ESR spectra contain the information not only on radicals' concentration but also on their structure and adjacent elements, such as the g value and the peak-to-peak linewidth of the first derivative signal. Studies have tried to correlate these parameters with the rank and constituents of coals as well as the coal conversion products [18–22,23]. It was found that each of these parameters is a combination of that of all the radicals presented in a sample but the value is determined mainly by the dominant radicals. In general, these parameters decrease with rising coal rank and intensity of reaction conditions. The decreases in these parameters were attributed to the removal of heteroatoms from the sample, mainly oxygen, and to the growth and ordering of aromatic structures. However, few researches [17] were reported on changes in g value and linewidth of radicals observed in the reaction of volatiles.

The above analyses suggest that the quality and yield of tars obtained from pyrolysis of coals are mainly determined by the reaction of volatiles. To inhibit the formation of heavy components, especially coke, in tars better understanding of the radicals' information associated with the reaction of volatiles is much needed. Therefore, this article studies the reaction of volatiles generated from a low-rank bituminous coal and a lignite using a two-stage fixed reactor with emphasis on coke formation and radical information.

2. Materials and methods

2.1. Coal samples

The low-rank bituminous coal is Shenmu coal (SM) and the lignite is Hulunbeier (HLBE), all from China. They were ground and sieved to 32–

74 μm (500–200 mesh) in size, and dried at 110 °C under a vacuum for 15 h before the pyrolysis experiments. Their proximate analysis (following the China National Standard GB/T 212-2008) and ultimate analyses (following the China National Standard GB/T 214-2007 for sulfur content, GB/T 476-2008 for carbon and hydrogen contents, and GB/T 19228-2008 for nitrogen content, and the difference as the oxygen content) are shown in Table 1.

2.2. Pyrolysis experiments

The pyrolysis experiments were carried out in a two-stage fixed-bed quartz tube reactor of 25 mm in diameter and 360 mm in length. After the first-stage reactor was heated to 650 °C and the second-stage reactor was heated to a predetermined temperature (440, 540, 600, 650 or 700 °C), a quartz crucible loaded with 6 g coal was inserted into the first-stage reactor as shown in Fig. 1. The temperature of the coal was measured by a type K thermocouple inserted into the coal sample, which showed a heating rate of approximately 215 °C/min in the temperature range of 300–480 °C. When the coal sample reached 540 ± 5 °C the pyrolysis was ended by stopping the heating and opening the furnace, allowing the reactor to be cooled in the air. In the experiment, the reactor was purged with N_2 at a flow rate of 60, 160, 260, 160 or 650 ml/min, corresponding to a volatiles' residence time of 6.9, 4.2, 3, 2.2, or 1.5 s in the second stage, respectively. The effluent of the second-stage reactor was cooled to liquid N_2 temperature in two traps in series to collect the condensable products. It was found that more than 92% of tars were condensed in the first trap.

2.3. Coke formed on reactor wall and presented in tar

After the reaction, the quartz tube reactor was washed with THF and ethanol sequentially, and then dried in the air. The dried reactor was filled with oxygen, sealed and heated to 500 °C for 10 min to burn the coke formed on the wall into CO_2. Since the amount of oxygen in the reactor was in excess of the coke, the combustion was complete. The quantity of CO_2 in the reactor was determined by a GC–MS, which is the same in mole as that of C in coke.

After each reaction, the cold traps were washed 3 times with 15 ml THF. The solution was filtrated with a filter membrane of 0.2 μm in pore. The residue on the membrane was then washed with 2 ml THF and ethanol sequentially before being dried at 40 °C under a vacuum for 3 h. The mass of residue was determined as the mass difference between the residue loaded membrane and the membrane subjected to the same THF-and-ethanol washing and drying operations. The final residue is the coke entrained in the effluent of the second-stage reactor and collected in tars.

2.4. ESR measurements

The tars collected from the pyrolysis experiments were sampled by glass capillaries of 1 mm in diameter. Each of the capillaries was loaded with approximately 5 ± 0.05 mg tar and sealed in a glass tube of 2 mm in diameter in a N_2 atmosphere. The glass tube was then inserted into a quartz tube of 4 mm in diameter and 250 mm in length for ESR (A200 Bruker) analysis. The ESR was operated at 9.5 GHz and 0.998 mW

Table 1
Proximate and ultimate analyses of the two coals.

Coal	Proximate analysis (wt.%)			Ultimate analysis (wt.%, daf)				
	Mad	Aad	Vad	C	H	O[a]	N	S
SM	7.7	8.1	36.5	78.6	4.6	15.2	1.1	0.5
HLBE	23.0	12.4	46.7	74.2	3.1	20.9	1.3	0.5

ad: air-dry basis; daf: dry-and-ash-free basis.
[a] By difference.