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Full Length Article

Nitrogen/NO conversion characteristics of coal chars prepared using different pyrolysis procedures under combustion conditions

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ABSTRACT

In actual combustion facilities, coal chars are often generated using a variety of pyrolysis processes, such as secondary pyrolysis, which is characterized by a long residence time in high temperature zone. The effects of such processes on the conversion of char N to NO during combustion have seldom been explored. In this study, the releases of NO during the combustion of coal chars obtained from different pyrolysis processes in a drop tube and in a fixed bed reactor were investigated. In addition, the extent of char N/NO conversion was studied in relation to the char reactivity, pore surface structure and carbon conversion in a horizontal tube furnace. The results show that, compared with chars generated by a single pyrolysis, chars treated by a subsequent secondary pyrolysis process exhibit larger pore surface areas but less reactivity because of the thermal annealing resulting from a longer thermal history. Chars with higher intrinsic reactivity were also found to release a lower amount of NO. However, a weak correlation was identified between the apparent reactivity and char N/NO conversion, indicating that intrinsic reactivity is more important and directly determines the NO reduction process under combustion conditions. Moreover, char N/NO conversion was significantly affected by the coal rank, and a greater extent of conversion of char N to NO was observed in the case of high-rank coal chars. At a high combustion temperature (1373 K), variations in the bulk O_2 concentration had little effect on the char N/NO conversion, and an apparent correlation was found between the extents of char N/NO conversion and the accessible pore surface area. These results indicate that at high temperatures, the char N/NO conversion is directly determined by the accessible pore surface area due to transportation limitations. The NO/(CO + CO_2) ratio increased with increasing burn-off in the latter stages of char conversion, which can be attributed to decreases in both the BET surface area and accessible pore surface area available for NO reduction during combustion.

1. Introduction

The subject of nitrogen oxide (NO_x) emissions has captured the interest of both researchers and the general public because of the serious environmental impact of these compounds. In modern pulverized coal (PC) combustion systems, fuel-fixed nitrogen (fuel N) is typically the major source of total NO_x emissions, and previous studies [1–3] have identified the processes by which nitrogen in either volatiles or char is converted to NO_x.

Volatile nitrogen has been shown to form HCN, NH_3, and soot-bound nitrogen as intermediate species during the pyrolysis process, all of which can be oxidized to NO_x or react with NO_x to produce N_2 under a reducing atmosphere. In addition, a significant portion of char N can be directly oxidized to NO_x. In modern low NO_x combustion systems, such as PC systems or fluidized bed (FB) coal combustion systems, volatile nitrogen is transformed into N_2 using a precisely controlled reducing atmosphere; as a result, char nitrogen has been identified as the main contributor to the furnace exit NO_x emissions [4].

The conversion process of nitrogen in chars is complex at PC combustion temperatures (which are higher than those used during FB combustion) because the concentrations of both reactants and products in the gas phase vary with the depth of their penetration into char pores, a depth that changes with char conversion. The transformation of char nitrogen to NO_x is believed to proceed via the formation of NO_x during char combustion, followed by the heterogeneous reduction of this NO_x by carbon [5]. However, the simultaneous occurrence of oxidation and reduction reactions makes it difficult to distinguish the contribution of each route to the net conversion of char N to NO_x. Several studies [3,6–8] have shown that coal char combustion conditions (such as reaction temperature, bulk oxygen concentration, and particle size) and factors related to the coal type (such as coal rank, char pore structure, char reactivity, nitrogen and ash level in the char) can

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greatly affect emission of NO_x during char combustion. In these previous experimental works, chars were specially prepared by pyrolysis procedures; thus, some factors related to pyrolysis, such as the temperature, heating rate, residence time, atmosphere and reactor pressure, are likely to have affected the extent of NO_x evolution [9–13].

In these studies, coal chars were typically prepared via a single high-temperature pyrolysis of coal, followed by cooling to ambient temperature. However, secondary pyrolysis chars undergo high-temperature pyrolysis more than once; such a process can significantly affect char reactivity through thermal annealing [14,15], although this effect has rarely been considered when assessing char N conversion. Note that heat treatment processes are known as reheating and/or re-cooling during original or secondary deep pyrolysis can greatly affect the pores and thus influence the apparent reactivity of the char [16].

At low combustion temperatures, micropores account for approximately 95% of the total reactive surface area and play a substantial role in the reactivity of char particles, while larger pores (mesopores and macro pores) provide channels for reactant gas transportation and directly affect the reaction rate at relatively high temperatures [17]. The char reactivity is also very sensitive to the heat treatment and preparation conditions; thus, the reactivity of chars can differ significantly, even when they originate from the same parent coal [18]. A study [19] by Arenillas investigated the effect of char structures obtained under various pyrolysis conditions on the reactivity and NO emissions. The results showed that an increase in the availability of active surface sites improved the apparent reactivity of the char, both for oxygen and for other reactive gases, in particular, NO.

In term of the path of char-N/NO conversion especially at high temperature (approximately over FB reaction temperature), the heterogeneous mechanisms are significant to determine the NO formation, so the physical diffusion of O_2 and NO in the pore may play an important role in NO formation because the reduction of NO mostly occurs on the pore surface. Previous studies mostly lay emphasis on the effect of the mass transfer limitations on combustion. However, few studies show the relationship between the diffusion of O_2 and NO and the final NO formation. Arana [9] proposed the first order reaction model assumed with respect to NO to calculate the effectiveness factor associated to the pore diffusion using a simple reaction-transport model. But there were significant differences in values of the NO diffusion coefficient, so he reported that it is possible that there exist two different length scales of relevance correspond to NO transport in macropores or micropores. Recently, Xu [20] reported that the influence of O_2 diffusion in the pore on NO reduction was similar to NO diffusion, so the depth of O_2 diffusion directly affected the accessible surface area and reduction time when NO diffused from the internal surface area to the external. In that paper, the O_2 diffusion was chartered by the effectiveness factor which was established by experimental data using first order reaction model and the experimental results of char-N/NO conversion were well explained.

The present study focused on the effects of char preparation under different pyrolysis conditions on the conversion of char N to NO. Ordinary pyrolysis, fast secondary pyrolysis, and slow secondary pyrolysis were all performed to prepare test batches of char, which were found to exhibit varying reactive characteristics and pore structures. The extent of char N/NO conversion was ascertained in each case to evaluate the effects of the char reactivity and pore texture on NO release during high-temperature oxidization.

2. Experimental section

2.1. Char sample preparation

Coal specimens were obtained from sources in China and had two different ranks and particles sizes in the range of 96–125 μm (a bituminous coal, denoted as type J, and a lignite coal, type Y). Various pyrolysis conditions were subsequently used to obtain chars with different reactivities and textural properties. First, standard pyrolysis char was obtained in a drop tube furnace under an inert atmosphere at 1173 K and with a residence time of approximately 2 s. A schematic diagram of this reactor has been previously published [21]. The resulting material is denoted as “original” char and was used to prepare two other types of char. After formation, this original char was quickly pushed into the center of a horizontal tube furnace (HTF) reactor (the apparatus discussed in Section 2.4) that had been preheated to 1373 K. After 30 min of residence time in this furnace, the char was promptly moved to the cooling section and cooled to ambient temperature using a water flow. This procedure is denoted as “fast secondary pyrolysis”, and the resulting material is termed fast secondary pyrolysis char. In an additional procedure, the original char was placed in the center of the HTF reactor at room temperature in advance and then heated to 1373 K at a constant rate of 10 K/min. A hold time of 30 min was applied when the reactor was at 1373 K, after which the char was pushed out to the cooling section and then cooled in preparation for collection in the same manner as that for the fast secondary pyrolysis char. This procedure is denoted as “slow secondary pyrolysis”, and the obtained char is termed “slow secondary pyrolysis char”. All of the above-described pyrolysis procedures were performed under an inert N_2 atmosphere. Proximate and ultimate analysis of data for all of the prepared char samples are provided in Table 1, and the heat treatment details are summarized in Table 2. Measurements and tests were subsequently performed to obtain the pore structure parameters and reactivity of the prepared chars.

2.2. Pore structure characterization

Coal char is a typical porous material and contains micropores (less than 2 nm), mesopores (2–50 nm) and macropores (more than 50 nm). The Brunauer–Emmett–Teller (BET) surface areas and porosities of the

Table 1
Proximate and Ultimate Analysis Data for the Two Original Parent Coals and their Chars.

Samples	Proximate analysis (wt% db)			Ultimate analysis (wt% d)					Diameter (μm)[c]	N/C atomic ratio
	VM	FC	Ash	C	H	N	S	O[b]		
Coal J	23.47	41.84	34.69	49.82	3.28	1.03	0.93	10.25	–	0.021
Char J_O	6.44	44.44	49.11	45.86	0.81	1.04	0.76	2.42	85.5	0.027
Char J_F	1.54	47.18	51.10	45.79	0.17	0.74	0.83	1.37	89.1	0.016
Char J_S	1.71	45.23	52.88	44.66	0.18	0.81	0.85	0.62	95.8	0.018
Coal Y	29.45	28.68	41.87	40.36	3.29	0.74	1.19	12.55	–	0.0183
Char Y_O	8.84	40.45	51.08	43.97	0.84	0.99	1.07	2.05	103.6	0.023
Char Y_F	2.95	42.01	55.04	41.74	0.18	0.74	1.39	0.91	104.3	0.017
Char Y_S	3.07	40.86	58.07	39.06	0.16	0.72	1.45	0.54	104.9	0.037

[a] Subscripts O, F and S represent the original, fast secondary pyrolysis and slow secondary pyrolysis char samples, respectively.

[b] Calculated by the difference.

[c] Average diameter of char particles.