Homogeneous and heterogeneous contributions of CO_2 and recycled NO to NO emission difference between air and oxy-coal combustion

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ABSTRACT

High concentration of CO_2 and recycled NO-containing flue gas are known to affect the total NO emission during oxy-coal combustion through both homogeneous and heterogeneous reactions. To evaluate each contribution, this work investigated the NO emission behavior in air and oxy-coal combustion atmosphere (O_2/CO_2 and O_2/recycled flue gas) with three different oxygen concentrations (21%, 27% and 32%). Three typical Chinese coals and their derived chars were employed and all of the experiments were conducted in a drop tube furnace at a temperature of 1373 K. The results show that the conversion ratio of coal nitrogen (coal-N) to NO increased with decreasing coal rank in all atmospheres. The NO emission rate in oxy-coal was lower than that in air combustion. The heterogeneous effect of CO_2 mitigated NO emission in oxy-coal combustion, whereas homogeneous contribution of CO_2 may have increased NO formation due to a great amount of coal-N was released in the form of volatile nitrogen (volatile-N) at a high concentration of CO_2. The reduction of recycled NO was the major reason for the lower NO emission in oxy-coal combustion, but the main removal route differed. The reduction of recycled NO through homogeneous reactions was more important for both the lignite and the high volatile content bituminous coal, whereas the heterogeneous reactions were more important for the anthracite NO removal.

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1. Introduction

Coal-fired power plants provide more than 70% of the electricity in China [1] but cause serious environmental issues such as global warming. Oxy-coal combustion technology, which uses pure O_2 and recycled flue gas (RFG) (mainly composed of CO_2) as a substitute for air, has been proven to be a promising way to control CO_2 emission from coal fired plants. The CO_2 may account for 95% (vol/vol) of flue gas during oxy-coal combustion, which afterwards can be captured economically and effectively [2–4]. It is worth noting that the pollutant emissions, e.g., NO_x, in oxy-coal combustion may differ from those in air combustion because recycled flue gas is used instead of N_2. Compared with air combustion, the NO emission in oxy-coal combustion with flue gas recycling is affected by the high concentration of CO_2 and recycled NO in the furnace [5,6].

Compared with the case of air combustion, the amount and composition of volatile nitrogen (volatile-N) would change in oxy-coal atmosphere due to the high concentration of CO_2. According to Sowa et al.'s experimental results ranged from 1600

to 1900 K, an American sub-bituminous coal released more volatile-N at a resident time of 15 ms in pure CO_2 than that in N_2 [7]. Duan et al. [8,9] found that during long residence time devolatilization (>150 s), CO_2 enhanced the conversion rate of coal nitrogen (coal-N) to volatile-N by releasing more HCN and less NH_3. Various possible reaction schematics are summarized in Table 1 from the reported literatures [5,8,10–14]. In regards to the influence of homogeneous impact of CO_2, Eq. (1) is thought to be the key factor because it changes the compositions of the O/H/OH radical pool. As a result, these composition changes could weaken NO formation from volatile-N [11,12]. The heterogeneous reactions between char nitrogen (char-N) and CO_2 could generate N_2 [14] or HCN [8] rather than NO in oxidation atmosphere. These reactions may decrease the amount of direct NO generation from char-N. It is not difficult to find that CO_2 could influence coal-N transformation through both homogeneous and heterogeneous reactions. However, the specific contribution of them is unknown.

Furthermore, recycled NO could also be reduced in the furnace by reacting with different reactants through homogeneous and heterogeneous reactions [5,13] (Table 1). NO reacts with hydrocarbons (CH_i), which are released at the beginning of devolatilization to form cyanide and amine intermediates (XN) through Eq. (2). NO converts into N_2 by reacting with XN as well, which is shown in

Table 1
Detailed influence of CO_2 and recycled NO on nitrogen transformation [5,8,10–14].

		High concentration of CO_2	Recycled NO
Homogeneous	Direct	$N + CO_2 \rightarrow NO + CO$ $NH_2 + CO_2 \rightarrow products$	$NO + CH_i$ (hydrocarbon radicals) $\rightarrow XN(HCN\ or\ NH_3) + CO/CO_2$ (2) $NO + XN \rightarrow N_2 + CO/CO_2 + H_2O$ (3)
	Indirect	O/H/OH radical pool is affected by $CO_2 + H \Longleftrightarrow CO + OH$ (1) Influence the following fate of HCN and NH_3	
	Direct	Char-N + $CO_2 \rightarrow N_2$/HCN + CO	$NO + char\text{-}N \rightarrow N_2 + CO/CO_2$ (4)
Heterogeneous	Indirect	$2NO + 2CO \rightarrow N_2 + 2CO_2$ on the char surface	The conversion of char-N to NO is suppressed in the presence of NO

Eq. (3). Meanwhile, NO is reduced to N_2 by the residual char, as shown in Eq. (4). Okazaki and Ando [5] found homogeneous NO removal reductions are more important than heterogeneous reactions for reducing NO exhaust during their experiment. In contrast, Hashemi et al. proposed a conclusion that heterogeneous NO removal reactions are more important [15]. Thus, the major recycled NO reduction route is still under debate. It is also necessary to determine the proportions of recycled NO homogeneous and heterogeneous removal for further NO controlling.

To solve the problems mentioned above, the detailed contributions of homogeneous and heterogeneous effects of high concentration of CO_2 and recycled NO were classified in the present work. Three types of Chinese coals were used as raw samples. Devolatilization tests in both air and oxy-coal conditions were performed first. Based on the combustion of coal and derived char at 1373 K, the homogeneous and heterogeneous contributions of CO_2 and recycled NO were quantified, respectively.

2. Experimental

Three types of Chinese coals (lignite, bituminous and anthracite) with a grain diameter of 45–100 μm were used for this investigation through a drop-tube furnace (DTF). The ultimate and proximate analysis of parent coals and derived chars are presented in Table 2. To simulate the devolatilization in air and oxy-coal conditions, the coal samples were first devolatilized in pure N_2 and CO_2, respectively, at 1373 K, and the solid products were labeled as N_2-char and CO_2-char. Each coal sample was combusted in the same DTF in O_2/N_2 or oxy-coal atmosphere (O_2/CO_2 and O_2/RFG) at 1373 K with three different O_2 fractions (OF = 21%, 27% and 32% by volume). O_2/CO_2 was used as one-through oxy-coal combustion atmosphere to distinguish the impact of the CO_2 and the recycled NO. The method from Yoshiie et al. [16] was employed to simulate the recirculated flue gas in O_2/RFG atmosphere.

Whereas the effect of N_2O was ignored and only NO was recycled in the present study. N_2-char was combusted only in air condition, and CO_2-char was combusted in oxy-coal condition to study char-N evolution. The coal feeding rate was 0.3 g/min. The char feeding rate was determined based on its Al element content to ensure the Al element feeding rate was equivalent to the parent coal feeding rate. The feeding rates of N_2-char and CO_2-char for the lignite, bituminous coal and anthracite were 0.13, 0.05, 0.14, 0.05, 0.27 and 0.26 g/min, respectively. The detailed parameters of the DTF can be found in our previous study [17]. The total inlet gas flow rate in the DTF was 5000 mL/min in both combustion and devolatilization processes to ensure the consistent residence time (approximately 2 s).

Gas samples were monitored by two gas analyzers following removal of dust and water. A Madur gas analyzer was used to detect CO and CO_2 by the non-dispersed infra-red (NDIR) method and O_2 by the electrochemical method. The other gas analyzer was used to detect NO by an electrochemical sensor over a range of 0–5000 ppmv (parts per million by volume). Nearly all of the coal-N was released due to the burnt out ratio of the samples was generally higher than 97% in the study. Since no HCN or NH_3 has been detected, the other major form of product containing N (except NO) during the combustion is N_2.

3. Results and discussion

3.1. Influence of CO_2 on char yield and nitrogen distribution

To verify the influence of CO_2 on coal-N evolution, the char yield and nitrogen distribution during devolatilization should be addressed first. Char yields were determined by mass conservation of elemental aluminum during the experiment [18]. Al contents of coal and char were tested by X-ray fluorescence (XRF).

Table 2
Properties of coals and the derived chars.

	Lignite	Lignite N_2-char	Lignite CO_2-char	Bituminous	Bituminous N_2-char	Bituminous CO_2-char	Anthracite	Anthracite N_2-char	Anthracite CO_2-char
Proximate analysis (air dried basis, wt.%)									
M	4.30	3.42	1.63	4.44	2.63	2.24	3.86	2.29	1.56
A	14.43	28.70	67.31	7.46	17.39	40.27	29.26	31.43	33.21
V	37.18	12.70	11.10	31.70	10.12	8.97	7.68	3.21	2.43
FC	44.09	55.18	19.96	56.40	69.86	42.31	59.20	62.07	60.80
Ultimate analysis (air dried basis, wt.%)									
C	56.61	59.28	23.94	67.64	61.80	46.12	59.95	63.94	62.92
H	5.42	0.62	0.34	3.65	0.68	0.43	1.20	0.57	0.67
N	0.82	0.63	0.23	0.80	0.56	0.29	0.92	0.91	0.81
S + O	18.42	7.35	6.55	16.01	16.94	10.65	4.81	0.86	0.83
Content of Al in ash by XRF (air dried basis, wt.%)									
Al	12.47	14.99	17.32	14.34	13.21	16.6	26.87	27.31	27.50

M, moisture; A, ash; V, volatile matter; FC, fixed carbon.