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Effects of Flue Gas Recirculation on NO and N₂O formations in Coal Combustion

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1. Introduction

Oxy-fuel coal combustion with flue gas re-circulation is known to be one of promising methods to reduce CO₂ emission from pulverized coal combustion power plants. In oxy-fuel system, combustion atmosphere consist of only O₂ separated from air and flue gas re-circulated from a stack. And then, the flue gas is dominated by CO₂ without any nitrogen. It is the most attractive point of oxy-fuel coal combustion to achieve CCS (Carbon Capture & Storage) system, which is a quick-impact approach to reduce CO₂ emission. In oxy-fuel system, several minor components in flue gas were re-circulated to the combustion zone together with CO₂. Effects of these additional impurities on flue gas composition are of our concerns. In this study, NO and N₂O emissions were experimentally observed in CO₂-O₂ coal combustion atmosphere. NO and N₂O emissions were also estimated under a flue gas re-circulation condition, in which small amounts of NO and N₂O were repeatedly added to the inlet gas to simulate the oxy-fuel condition. Furthermore, elementary reaction kinetics for NO and N₂O formations was numerically analyzed under conditions identical to experiments.

2. Experimental and Numerical Analyses

Coal combustion experiments were conducted using a drop tube furnace equipped with an external electric heater, as shown in Fig. 1. It can be divided to three parts for fuel injection, reaction and sampling. Pulverized coal can be continuously fed into the reactor through this injector with entraining gas. Coal sample used in this study is bituminous coal from Australia, containing nitrogen of 1.47%. The reactor is made of quartz tube, having a length of 2m and an inner diameter of 40mm. The temperature in a reaction part is controlled by an external electric heater. Water-cooled sampling probe is inserted from the bottom of the reactor. Combustion gas in the reactor was sampled by this probe, and analyzed for gas composition and unburned carbon in particulates. Sampling point at the top of the probe was fixed in this study, and a distance between the injector and the top of sampling probe determined a residence time for coal combustion. Table 1 shows experimental conditions for air and CO₂-O₂ coal combustions. O₂ concentration was set to be 21 vol% under both air and CO₂-O₂ combustions. In general, O₂ concentration for oxy-

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fuel combustion should be increased to about 30% so that the same temperature field could be produced between oxy-fuel and air combustions. However, the reaction mechanism was of the most interest, while the combustion temperature can be kept constant by external electric heater in this study. Then, the O_2 concentration was the same between oxy-fuel and air combustions in this study. Oxygen fuel ratios were set to be 1.2 under all experimental conditions. Temperature range between 1073 and 1223K is relatively low, close to CFB combustion condition.

In oxy-fuel system, several minor components in flue gas were re-circulated to the combustion zone together with CO_2 . In this study, combustion atmosphere under oxy-fuel coal combustion condition was simulated focusing on only NO and N_2O as re-circulated impurities. Table 2 shows procedures to make up re-circulated gas with additional NO and N_2O . They were sequentially prepared with gas recycle times i after the last analysis of flue gas compositions. Other experimental conditions are same as those for CO_2 - O_2 combustion shown in Table 1. At first, CO_2 - O_2 combustion experiment was conducted and flue gas was analyzed for its composition. And then, the composition was copied to the inlet gas condition with additional O_2 at 1st flue gas re-circulation experiment. By these repetitions, inlet gas condition approaches to steady-state oxy-fuel condition with increase in gas recycle times.

Elemental reaction analysis was conducted on the basis of GRI-Mech ver.3.0 plus several surface reactions. It includes four solid-gas reactions, 52 chemical species and 323 elemental reaction formulas. Pressure and temperature were assumed to be constant through the reaction time. Fixed carbon in coal was assumed to consist of only C, and other elements were allocated to volatiles. Chemical species in volatiles from coal were assumed to be C_2H_4 , CO, H_2 , HCN and NH_3 , and their composition was determined as follows. N in coal was distributed to HCN and NH_3 at ratio of 1:1, and the rest of H in coal was distributed to C_2H_4 and H_2 at ratio of 1:1. Balance C was regarded as CO. Elemental composition of fuel coal and other combustion conditions are the same as those in experiments described above. In addition, a procedure to make up re-circulated gas in this simulation was in common with that in experiment shown in Table 2. Output under oxy-fuel combustion can be derived as a convergence after several recycling times.

3. Results and Discussion

Fig. 2(a) shows conversions of input N to NO with gas recycle times at 1073K. Conversions of input N to NO under flue gas re-circulation condition were found to be almost constant with gas recycle times, and they were lower than that under air condition. It means that NO in flue gas did not accumulate in spite of additional NO to inlet gas resulting from flue gas re-circulation. And NO emission under oxy-fuel combustion was smaller than that under air combustion.

Fig. 2(b) shows conversions of input N to N_2O with gas recycle times at 1073K. Conversions to N_2O under flue gas re-circulation condition were found to reach a steady state after increasing slightly, and they were higher than that under air condition. It means that N_2O in flue gas accumulated due to additional N_2O resulting from flue gas re-circulation. And N_2O emission under oxy-fuel combustion was larger than that under air combustion.

Fig. 3(a) shows variation of NO concentration with reaction time as a result of elemental reaction analysis. Initial NO concentrations under air and CO_2 - O_2 conditions are naturally zero, while initial NO concentration under oxy-fuel condition is equal to the value in flue gas diluted by oxygen. The line of NO concentration under oxy-fuel combustion condition is regarded as a convergence line after several gas recycles under flue gas re-circulation conditions. In all cases, combustion reaction progress drastically at about 500ms and terminate in short time. Simultaneously, NO concentrations increase to stable values after combustion reaction. NO concentrations after combustion reaction under CO_2 - O_2 condition are lower than that under air condition. In addition, NO concentration after combustion under oxy-fuel condition is almost the same as the value under CO_2 - O_2 condition. It means that NO accumulation doesn't happen in spite of flue gas re-circulation. These facts are consistent with the experimental results described in the previous section.

Fig. 3(b) shows variation of N_2O concentration with reaction time. N_2O concentrations drastically increase to stable values after combustion reaction as well as NO in Fig. 4(a). However, N_2O concentration after combustion reaction under CO_2 - O_2 condition is higher than that under air condition. It seems that N_2O accumulation happens due to the additional NO within several recycle times. Nonetheless, the accumulation behavior declines within several re-circulation times in this simulation. And then, the convergent concentration can be regarded as the N_2O concentration in the steady state under oxy-fuel condition. These facts are also consistent with the experimental results.

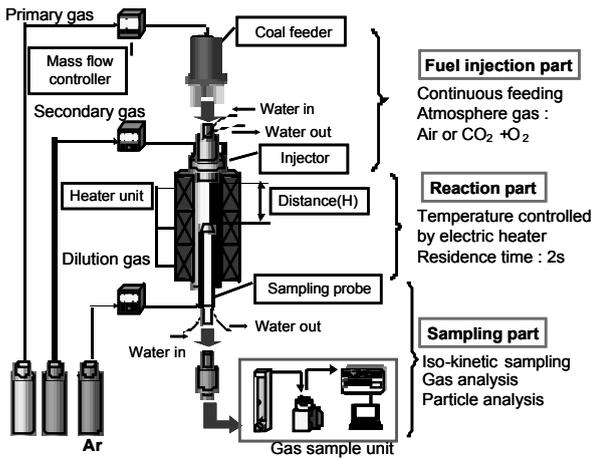


Table 2 Experimental conditions for CO₂-O₂ and air combustion

Atmosphere	CO ₂ +O ₂	Air
CO ₂ :O ₂	79:21	
Primary gas [L/min]	0.22 (O ₂) 0.83 (CO ₂)	1.05 (Air)
Secondary gas [L/min]	0.81 (O ₂) 3.04 (CO ₂)	3.85 (Air)
Dilution gas (Ar) [L/min]	1.20	
Dilution rate (Sample gas : Ar = 1 : 4)	5	
Stoichiometric air ratio	1.2	
Coal feed rate (g/min)	0.5 ± 0.05	
Mean particle size (μm)	2.320	
Sampling distance from injector [mm]	1300	
Furnace temperature [K]	1073 1123 1173 1223	
Residence time [s]	2	

Fig. 1 Schematic of drop tube furnace for coal combustion

Table 3 Concentrations of gas species in atmosphere simulating oxy-fuel coal combustion

i : recycle times ($i=0$ to 5)
 x_i : NO conc. in flue gas in i_{th} recycle experiment ($x_0=0$)
 y_i : N₂O conc. in flue gas in i_{th} recycle experiment ($y_0=0$)
 a : dilution ratio defined by additional O₂ to the flue gas

Gas	O ₂	NO	N ₂ O	CO ₂
Vol%	21	ax_{i-1}	ay_{i-1}	Balance

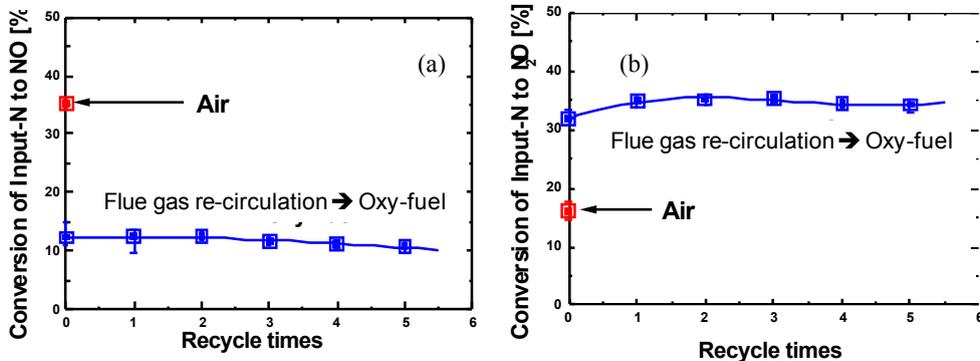


Fig. 2 Conversions of input N to (a) NO and (b) N₂O with gas recycle times at 1073K

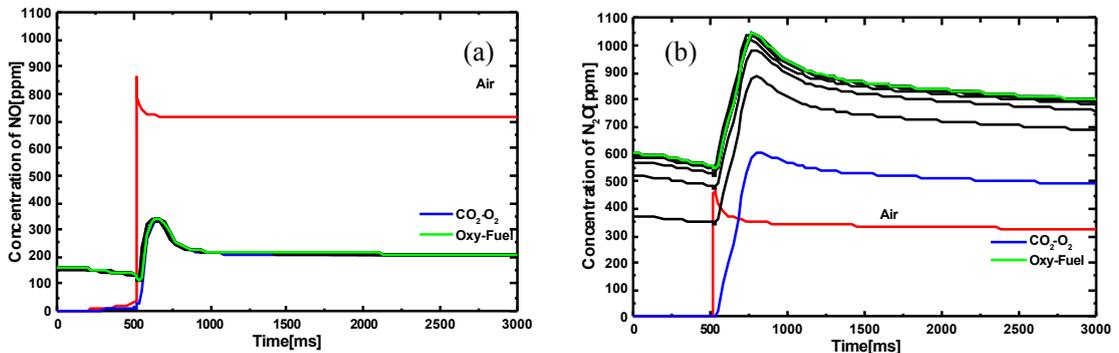


Fig. 3 Variations of (a) NO and (b) N₂O concentrations with reaction time under air, CO₂-O₂ and oxy-fuel combustion conditions