CO_2, NO_x and SO_2 emissions from the combustion of coal with high oxygen concentration gases

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CO_2, NO_x and SO_2 emissions from the combustion of coal with high oxygen concentration gases

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Abstract

The emissions of CO_2, NO_x and SO_2 from the combustion of a high-volatile coal with N_2- and CO_2-based, high O_2 concentration (20, 50, 80, 100%) inlet gases were investigated in an electrically heated up-flow-tube furnace at elevated gas temperatures (1123–1573 K). The fuel equivalence ratio, ϕ, was varied in the range of 0.4–1.6. Results showed that CO_2 concentrations in flue gas were higher than 95% for the processes with O_2 and CO_2-based inlet gases. NO_x emissions increased with ϕ under fuel-lean conditions, then declined dramatically after $\phi = 0.8$, and the peak values increased from about 1000 ppm for the air combustion process and 500 ppm for the O_2(20%) + CO_2(80%) inlet gas process to about 4500 ppm for the oxygen combustion process. When $\phi > 1.4$ the emissions decreased to the same level for different O_2 concentration inlet gas processes. On the other hand, NO_x emission indexes decreased monotonically with ϕ under both fuel-lean and fuel-rich combustion. SO_2 emissions increased with ϕ under fuel-lean conditions, then declined slightly after $\phi > 1.2$. Temperature has a large effect on the NO_x emission. Peak values of the NO_x emission increased by 50–70% for the N_2-based inlet gas processes and by 30–50% for the CO_2-based inlet gas process from 1123 to 1573 K. However, there was only a small effect of temperature on the SO_2 emission.

Keywords: Coal combustion; Pollutant emissions; High oxygen concentration gas

1. Introduction

Emissions of greenhouse gases, chiefly CO_2, by human way are the main contributors to the anticipated change in the climate. The largest source of CO_2 is the combustion of fossil fuels for power generation. On the third Conference of the Parties to the Framework Convention on Climate Change held in Kyoto in December 1997, the so-called Annex-1 countries agreed to reduce greenhouse emissions by 5% in the period 2008–2012 compared with the 1990 levels. As the global demand of energy, greatly dependent on fossil fuel, mainly being coal, is increasing, CO_2 discharge will further increase. It is necessary to recover CO_2 from flue gas in combustion processes and to use CO_2 to make products or for other useful purposes. However, the CO_2 concentration of the exhaust gas discharged from the present coal firing power plants is low because the combustion air contains only about 21% of oxygen and the remaining 79% mostly in the form of nitrogen is discharged as exhaust gas. The recovery of CO_2 from this flue gas is very costly.

A significant use of coal has serious consequences to generate large amount of pollutants. Among the pollutants the main ones are SO_2, a major contributor to acid rain, NO and NO_2, collectively called NO_x, which plays an important role for photochemical smog and acid rain. Considerable effort has been made and many techniques [1–6] have been developed to reduce the emission of NO_x and SO_2 from the combustion processes. Some of these techniques have been widely used in industry. However, a minimization of the pollutant emissions by these technologies is generally not compatible with high combustion efficiency. New cost-effective methods for further reduction of NO and SO_2 are needed to meet stricter requirements in the future.

Recently, the process of coal combustion with oxygen (CCO), which separates nitrogen from the combustion air in advance, has attracted special attention [7–13]. The concentration of CO_2 in the exhaust gas of this new process can reach 95% or higher [7] because nitrogen is separated from combustion air in advance. Compared with the conventional process of coal combustion with air (CCA), CCO process possesses the following advantages. (1) The recovery of CO_2 from exhaust gas will become easier and

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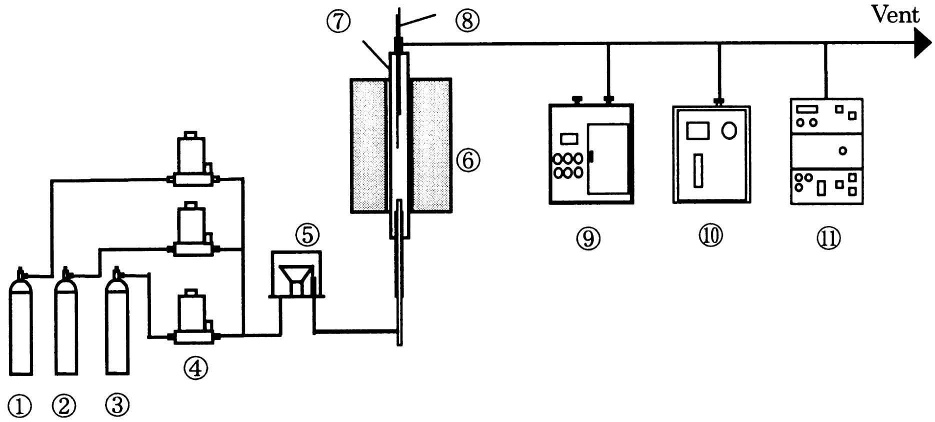

Fig. 1. The schematic drawing of the experimental apparatus.

less costly, and zero emission may even be realized in this process. (2) Combustion efficiency will be enhanced by higher concentration O_2 combustion and boiler efficiency will increase because the amount of exhaust gas is greatly reduced. (3) The amount of NO_x produced in combustion may be reduced because of the elimination of atmospheric nitrogen fixation to NO. (4) Combustion temperature can be controlled with the recirculation of part of the flue gas (chiefly CO_2), making the process more flexible in operation and coal rank.

The aim of the present study is to make some fundamental experiments on this new process, including the effects of the concentration of oxygen in the inlet gas and other operation conditions on the emissions of CO_2, SO_2, NO_x. In the experiments, besides pure oxygen, $O_2 + N_2$ and $O_2 + CO_2$ with different O_2 concentration were used as inlet gases. $O_2 + N_2$ was selected for comparing with the CCA process and examining the effect of N_2 in inlet gas on the pollutant emissions. $O_2 + CO_2$ was selected for simulating the process of flue gas recirculation. This fundamental research will be helpful to understand and develop this new combustion process.

2. Experimental

A schematic drawing of the experimental, quasi-one-dimensional, electrically heated combustor and its flow system is shown in Fig. 1. The combustion chamber consisted of a cylindrical alumina tube with an inner diameter of 28 mm, which was heated by a SiC element. The heated part was 300 mm long. Four Pt/Pt–13%Rh thermocouples were placed at different positions along the axis of the tube. The feed gases were supplied from gas cylinders and regulated by mass flow controllers. Pulverized coal was supplied continuously by an ultrasonic feeder and sent pneumatically by the feed gas to the combustion zone from the bottom of the tube. The properties of the used coal are given in Table 1. The coal feed rate was up to 180 g/h. The total inlet gas flow rate was controlled between 1.0 and 1.5N l/min in the experiments to maintain the gas resident time of 2 s at different temperatures. The expected concentration was realized by changing the O_2 and base gases (N_2 or CO_2) flow rate. Because of the small size of coal particles, high volatile matter and low ash content (2%), the slip velocity between gas and unburned coal or char was so small that the resident time of the particles was nearly the same as that of the gas. This resident time is similar to those in industrial furnaces.

The exhaust gas composition was determined using an on-line gas chromatography for O_2, CO, CO_2, N_2, a chemiluminescent analyzer for NO and NO_2, and a SO_2 analyzer. These instruments were calibrated periodically by injecting standard gases, respectively.

Table 1
The properties of coal

Size (μ)	Proximate (wt%, db)			Ultimate (wt%, daf)				
	FC	VM	Ash	C	H	N	S	O
60–125	50.0	48.0	2.0	73.5	5.2	1.4	1.1	18.8

3. Results and discussion

3.1. Flue gas composition

Fig. 2 shows the concentrations of O_2, CO_2, N_2 and CO in flue gases as functions of fuel equivalence ratio, ϕ, at

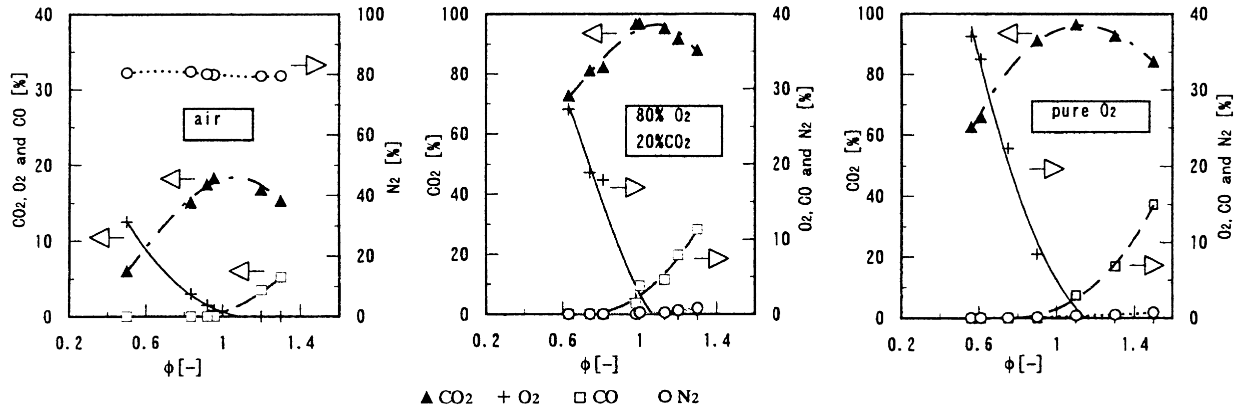

Fig. 2. The variations of O_2, CO_2, N_2 and CO in flue gas with fuel equivalence ratio at 1273 K.

1273 K for the CCO, CCA and $O_2 + CO_2$ processes. As shown in Fig. 2, in the fuel-lean combustion, CO_2 concentration increased with ϕ, on the other hand, in the fuel-rich combustion, CO_2 concentration decreased with ϕ as CO was produced increasingly. The peak of CO_2 concentration was only about 16% for the CCA process, it was, however, more than 95% for the CCO process and the $O_2 + CO_2$ process (both are called as N_2-free processes). N_2 concentration in flue gas for the CCA process maintained as high as 80%, but for the N_2-free processes it was only less than 1%, mainly derived from the fuel-nitrogen in coal. High CO_2 concentration can make the recovery of CO_2 from the N_2-free process more efficient than from the traditional CCA process. In addition, the concentration of O_2 decreased largely as equivalence ratio increased in the fuel-lean combustion, but at the same equivalence ratio O_2 concentration for the CCO process was much higher than that for the CCA and $O_2 + CO_2$ processes. Experiments at other temperatures of 1123, 1423 and 1573 K showed the same results on flue gas composition.

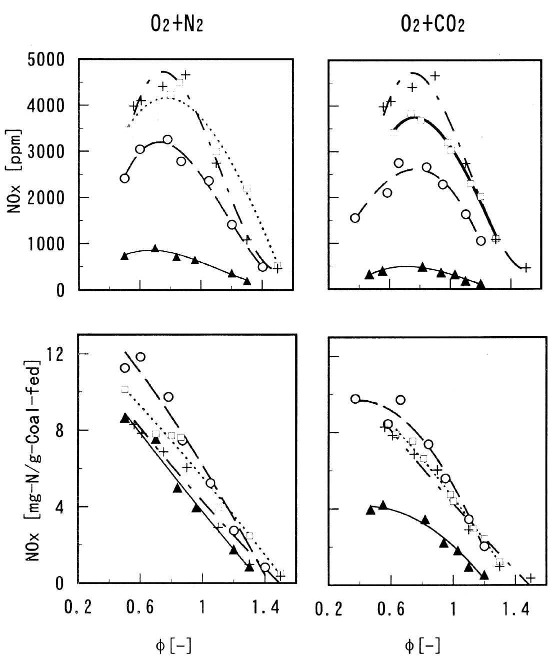

Fig. 3. NO_x emission versus fuel equivalence ratio at different O_2 concentrations for N_2- and CO_2-base inlet gases at 1273 K.

3.2. NO_x emissions

Fig. 3 shows NO_x emissions versus fuel equivalence ratio at different O_2 concentrations for N_2- and CO_2-based inlet gases at 1273 K, expressed in ppm and mg-N/g-Coal-fed at the upper and lower rows, respectively. In all the cases the emitted NO_x content (ppm) in flue gases increased initially with ϕ in the fuel-lean region, and then declined dramatically as ϕ approached and exceeded the stoichiometric point (fuel-rich region). A similar trend was reported for the air process by other researchers [14–16]. The peaks of NO_x were at an equivalence ratio of around 0.8 for all the kinds of inlet gases used in the experiments. The NO_x concentration at peak decreased as the O_2 concentration in inlet gas decreased, from as high as 4500 ppm for the pure oxygen process to less than 1000 ppm for the air process, and to about 500 ppm for the $O_2(20\%) + CO_2(80\%)$ inlet gas combustion process. However, NO_x emission indexes (mg-N/g-Coal-fed) monotonically decreased with the increase of ϕ in both fuel-lean and fuel-rich combustion, as shown in the lower row of Fig. 3. A similar trend was reported by Courtemanche et al. [15] in the combustion of coal and man-made organic materials with air. In the fuel-lean combustion, the low ratio of coal to inlet gas led to low NO_x content in flue gas; but due to the oxidizing atmosphere more fuel-N conversion to NO_x, resulting in a high NO_x emission index. The further decline of NO_x emissions may be attributed to the reducing atmospheres that favored the formation of HCN and NH_3 [17,18] and the reduction of NO to molecular nitrogen by homogeneous and heterogeneous reaction [18–26]. Although NH_3 and HCN were not measured in the experiments, the explanation may be

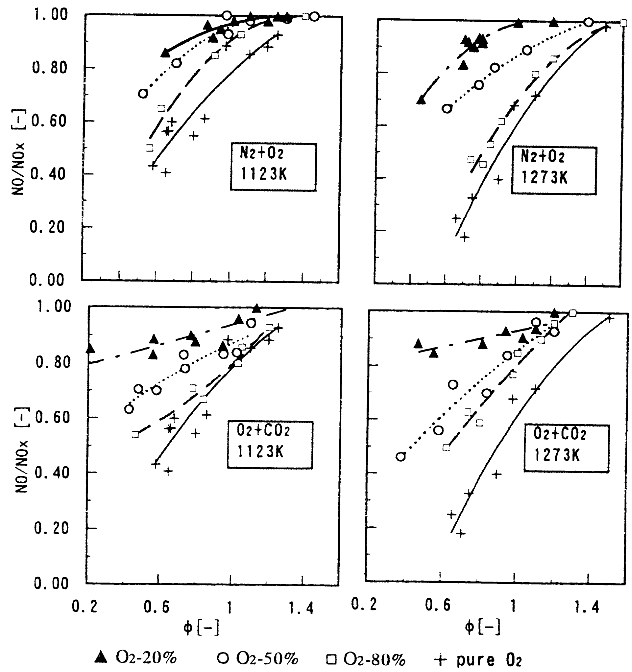

Fig. 4. The effect of fuel equivalence ratio and O_2 concentration on NO/NO_x for N_2- and CO_2-based inlet gases at 1123 and 1273 K.

confirmed by the appearance and the increase of CO and N_2 (for N_2-free inlet gas process), as shown in Fig. 2. Particularly, NO_x concentration in flue gas for the processes with inlet gas of higher O_2 concentration decreased more quickly

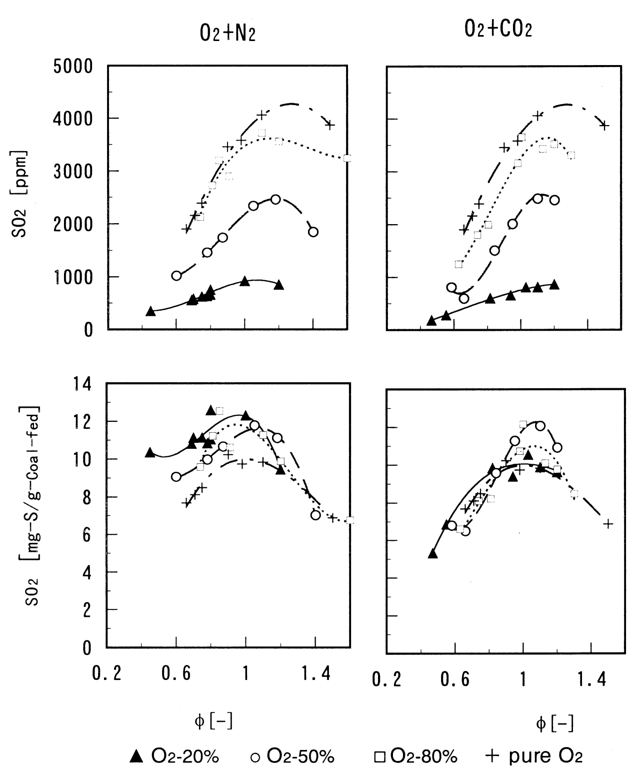

Fig. 5. SO_2 emission versus fuel equivalence ratio at different O_2 concentrations for N_2- and CO_2-based inlet gases at 1273 K.

after the peak and approached as low as that of the processes with lower O_2 concentration inlet gas when $\phi > 1.4$. This evidence implies that such NO_x emission controlling technology as staged combustion [2,3], which has been widely used in the CCA process in industry, can be introduced to CCO and O_2 + flue gas recirculation processes. The NO_x concentration may reach the same level as the CCA process so that the amount of NO_x emission will be largely reduced.

Comparing the two columns of Fig. 3, NO_x emissions both in ppm and in mg-N/g-Coal-fed for the CO_2-based inlet gases are always lower than those for the N_2-based inlet gases process at each O_2 concentration level. This is due to non-NO_x formation via fixation of atmospheric (molecular) nitrogen in CO_2-based gases, and/or the reduction of NO on char surface through the NO/CO/char reaction [7,23–26]. CO_2 previously existing in inlet gas reacted with coal and/or char in the beginning of combustion to produce CO in the experimental temperature region [27], which promoted the reduction of NO [24].

NO_x concentration in flue gas increased with the increase of O_2 concentration in inlet gases for both N- and CO_2-based inlet gases in the range of experimental equivalence ratio, as shown in the upper row of Fig. 3. However, as shown in the bottom row of Fig. 3, the NO_x emission indexes reached the highest level when O_2 concentration was 50% for both the N_2- and the CO_2-based processes, although the value for the CO_2-based inlet gas processes changed little with the O_2 concentration in inlet gas except for the $20\%O_2 + 80\%CO_2$ process. When O_2 concentration in inlet gases was higher than 50%, NO_x emission indexes decreased, and for the pure oxygen process it went even back to the same level as that of the air process.

In all the experiments in this paper, NO and NO_2 were simultaneously measured by the chemiluminescent analyzer. Fig. 4 shows the ratio of NO/NO_x in flue gas as a function of fuel equivalence ratio at different O_2 concentrations. The ratios for N_2-based inlet gas and CO_2-based inlet gas followed the same trend, as shown in Fig. 4. Under fuel-lean conditions the changes of NO/NO_x with equivalence ratio were quite different for the various O_2 concentration inlet gases. The NO/NO_x for the inlet gases with higher O_2 concentration decreased more quickly than that with lower O_2 concentration as equivalence ratio decreased. On the other hand, under fuel-rich conditions NO/NO_x for all the kinds of inlet gases approached 1.0 as ϕ increased. These results suggest that de-NOx operation for the CCO process should be reconsidered. Since NO/NO_2 ratio affects the consumption rate of de-NO_x reagent (NH_3) in the de-NO_x processes, i.e. consumption rate for NO_2 reduction with selective non-catalytic reduction approach will be 4/3 compared to NO reduction. The chemical reaction formulas are expressed as $4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O$ and $6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O$, respectively.

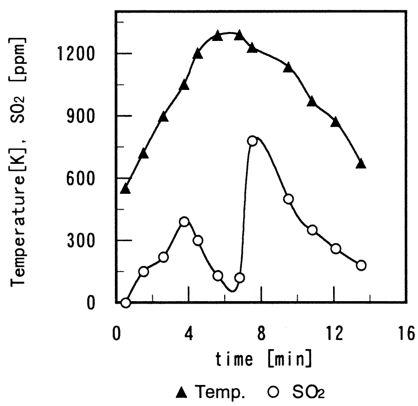

Fig. 6. Changes of temperature and SO_2 emission in batch combustion.

3.3. SO_2 emissions

Plots of the SO_2 emissions in the combustion processes versus equivalence ratio at different O_2 concentrations for N_2- and CO_2-based inlet gases are shown in Fig. 5. For both the N_2- and the CO_2-based inlet gas processes, SO_2 emissions in ppm increased with the equivalence ratio in fuel-lean region, as shown in the upper row of Fig. 5, and then appeared to slightly decrease after $\phi > 1.2$. The decrease of SO_2 emission in the fuel-rich region may partly be the result of the formation of other flurous matters such as H_2S, COS and CS_2 and reduction of SO_2 [28] in the reducing atmosphere. Experiments of coal combustion with oxygen in batch operation showed, as in Fig. 6, that there were two peaks of SO_2 emission in the combustion process. This means that there are two types of S in the coal: some of the S are volatile and others combined strongly with fixed-C in char. From this point, the retention of sulfur in char or unburned coal may be another important reason for the decrease of SO_2 emission in the fuel-rich region. Beer [29] and Chang [30] attributed the decrease of SO_2 emission to aluminosilicate components in ash, which favored retention of sulfur.

3.4. Gas temperature effect

The effects of gas temperature on NO_x emission for the N_2- and the CO_2-based inlet gas processes are shown, respectively, in Figs. 7 and 8. The results showed that NO_x emission increased with gas temperature for all the cases examined, the peak values increased by 50–70% for the N_2-based and 30–50% for the N_2-free processes when gas temperature increased from 1123 to 1573 K. The exception is the process with $20\%O_2 + 80\%CO_2$ inlet gas, in which NO_x emissions were very low at each temperature and increased by almost eight times from 1123 to1573 K. The explanation is that high concentration of CO_2 in inlet gas promoted the reaction of CO_2 with C to CO, and NO_x was reduced by CO even in the fuel-lean region especially at lower temperatures. It may be confirmed by the fact that CO

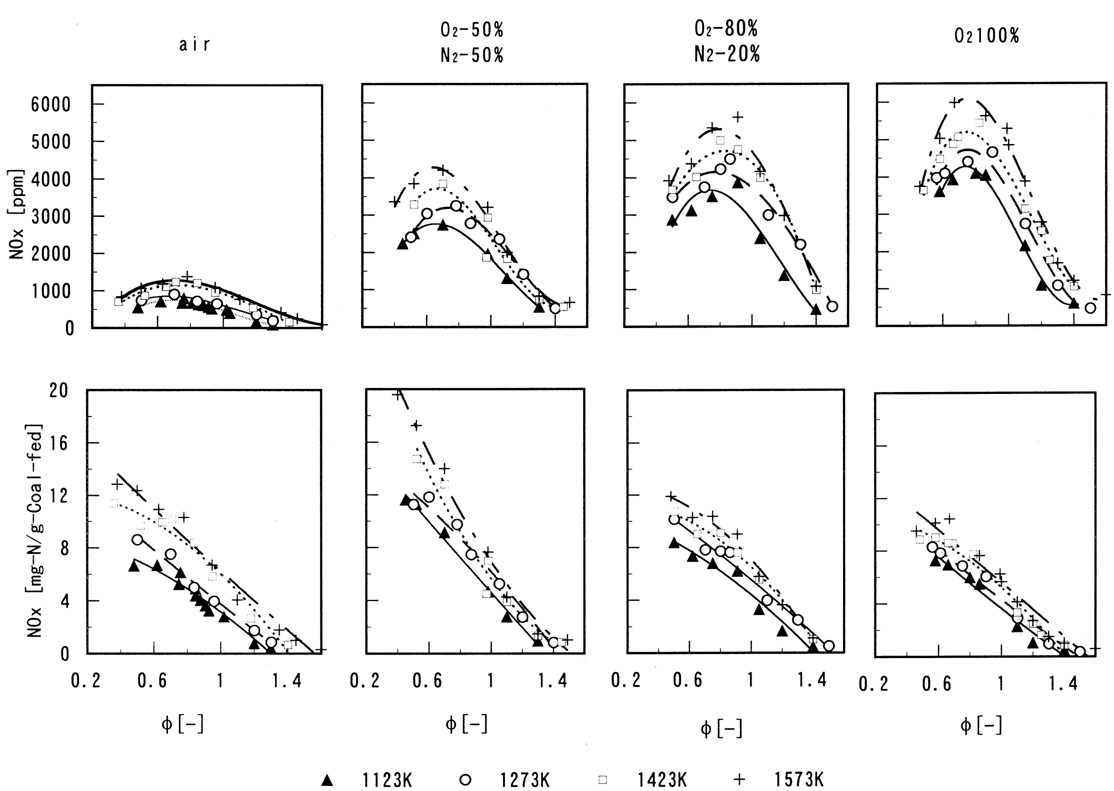

Fig. 7. NO_x emissions versus equivalence ratio and temperature at different O_2 concentration for N_2-based inlet gases.

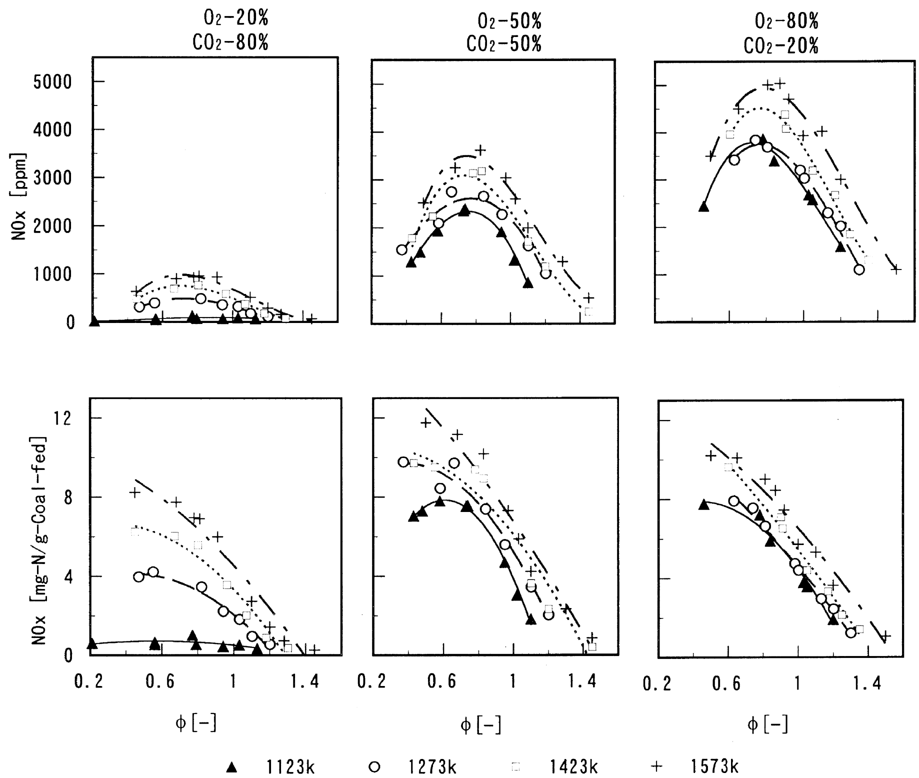

Fig. 8. NO_x emissions versus equivalence ratio and temperature at different O_2 concentration for CO_2-based inlet gases.

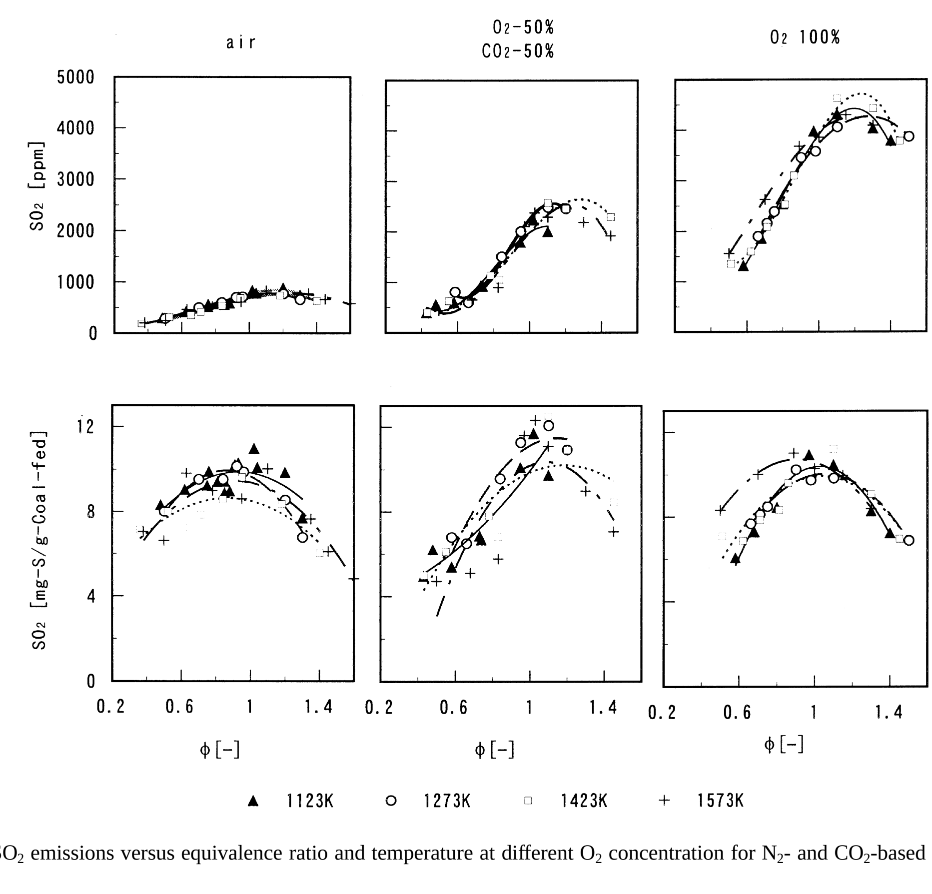

Fig. 9. SO_2 emissions versus equivalence ratio and temperature at different O_2 concentration for N_2- and CO_2-based inlet gases.

was detected at any ϕ in the experiments at 1123 K. Many researchers [15,31–35] reported the effects of temperature on NO_x emissions for CCA. Haussann and Kruger [33] reported that the release of fuel-nitrogen from coal increased by 30–40% with temperature in the same range of temperature as this paper. Courtemanche [15] reported NO_x emissions increased by up to 25% when gas temperature increased from 1300 to 1600 K in the combustion experiments of a high volatile bituminous coal with air.

In the fuel-rich region, NO_x emissions in the higher temperature processes decreased to the same level as those in the lower temperature processes at $\phi > 1.4$.

For the processes with the same O_2 concentration in inlet gas, NO_x emissions from the CO_2-based gas process were always lower than those from the process with N_2-based inlet gas for each temperature examined. And it can be further seen that the process with $50\%O_2 + 50\%N_2$ inlet gas emitted the most NO_x per unit of coal at any temperature. This can be explained that this inlet gas possessed high concentration of both O_2 and N_2, which promoted the thermal formation of NO_x from N_2 and the conversion of fuel-N to NO.

Fig. 9 presents the effects of gas temperature on SO_2 emissions for the air, the inlet gas of $50\%O_2 + 50\%CO_2$ and the pure O_2 processes. It is seen that there was a small effect of temperature on the SO_2 emissions for N_2-based, CO_2-based and pure oxygen processes.

4. Conclusion

1. CO_2 concentration in flue gas was only about 16% for the processes with air, but higher than 95% for the processes with N_2-free (O_2, $O_2 + CO_2$) inlet gas. Recovery of CO_2 from the N_2-free processes will be easier and more efficient than the traditional air processes.
2. NO_x emissions increased with ϕ in fuel-lean combustion and declined quickly as ϕ approached and exceeded the stoichiometric point. The peaks were at around $\phi = 0.8$ for all the cases in the experiments and the peak values increased from 1000 ppm for the air process and 500 ppm for the $O_2(20\%) + CO_2(80\%)$ inlet gas process to about 4500 ppm for the oxygen combustion process. When $\phi > 1.4$ NO_x emissions will decrease to the same level for all the inlet gas processes in this experiment. NO_x emission indexes decreased monotonically as ϕ increased under both fuel-lean and fuel-rich conditions. CO_2-based inlet gas processes emitted less NO_x than N_2-based inlet gas processes with same O_2 concentration in inlet gases. NO_x emissions reached highest level from the process with N_2-based inlet gas containing $50\%O_2$.
3. SO_2 emissions increased with ϕ in fuel-lean combustion and decreased slightly when $\phi > 1.2$.
4. There was a large effect of temperature on NO_x emission. NO_x emissions at peak increased by 50–70% for the N_2-based inlet gas processes and by 30–50% for the CO_2-based inlet gas processes from 1123 to 1573 K. NO_x emitted from higher temperature processes reached almost the same level as lower temperature processes when $\phi > 1.4$. On the other hand, temperature had little effect on SO_2 emissions.

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