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Article

Experimental Research on Heterogeneous N_2O Decomposition with Ash and Biomass Gasification Gas

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Abstract: In this paper, the promoting effects of ash and biomass gas reburning on N_2O decomposition were investigated based on a fluidized bed reactor, with the assessment of the influence of O_2 on N_2O decomposition with circulating ashes. Experimental results show that different metal oxides contained in ash play distinct roles in the process of N_2O decomposition with biomass gas reburning. Compared with other components in ash, CaO is proven to be very active and has the greatest promoting impact on N_2O decomposition. It is also found that O_2, even in small amounts, can weaken the promoting effect of ash on N_2O decomposition by using biomass gas reburning.

Keywords: heterogenous N_2O decomposition; circulating ash; CFB; biomass gas

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1. Introduction

With the popularization of fluidized bed technology, the nitrous oxide (N_2O) generated in the circulating fluidized bed (CFB) combustion process has aroused more and more attention. The concentration of N_2O emissions from CFB is in the range from 20 to 300 ppm and sometimes 400 ppm [1]. Compared with typical N_2O emissions from conventional pulverized coal-fired boilers (less than 10 ppm), it has becomes a serious problem that may represent an obstacle for the development of CFB boilers [2,3].

Heterogenous N_2O decomposition in CFB boilers indicates that heterogenous reactions must happen between N_2O and some components in solid fuels, ashes or catalysts [4,5]. In CFB power plants the ash consists of various sorts of oxides, such as SiO_2, Al_2O_3, Fe_2O_3 and CaO. The reaction mechanism of the promoting effect on N_2O decomposition with these oxides can be described as adsorbing and catalytic effects. On the one hand, some active radicals exist in the surface of solid oxides, which can absorb both H and OH. The decomposition of N_2O is then strengthened due to reactions such as $H + N_2O \leftrightarrow N_2 + OH$, $N_2O + H \leftrightarrow NH + NO$, $N_2O + H \leftrightarrow NNH + O$, $N_2O + H \leftrightarrow HNNO$ and $N_2O + OH \leftrightarrow N_2 + HO_2$. On the other hand, the conversion rate of the heterogenous decomposition of N_2O in the CFB increases owing to the catalytic effect of oxides [6–8].

Circulating ash can promote the decomposition of N_2O. The combustion of biomass, solid waste and coal in CFB can produce large amounts of ash. The influences of the different components in ash on N_2O decomposition vary a lot [9,10]. Ca, Fe, Al and other metal oxides in circulating ash are considered as active ingredients. The catalytic effect of circulating ash on N_2O decomposition depends highly on its specific surface area. The larger the specific surface of circulation ash is, the greater benefit for N_2O contacting with circulating ash. With the impact of circulating ash, a small amount of N_2O was converts to nitric oxide (NO) [11].

Shen *et al*. analyzed the promoting effect of char on N_2O decomposition in the temperature range of 677–977 °C [4], and the results showed that N_2O conversion rate was about 90% under the circumstance with the temperature 900 °C comparing with 60% in bare bed. Meanwhile, the authors analyzed the promoting effect of oxide and sulphate on N_2O decomposition in the temperature range of 677–977 °C, and it was found that the sequence of levels of the promoting effect was: $Fe_2O_3 > CaSO_4 > Al_2O_3 > SiO_2 > MgSO_4 > MgO >$ bare bed, with the conversion of N_2O being 99%, 91%, 81%, 69%, 59%, 47% and 39%, respectively [4]. With respect to the catalytic effect of these oxides, the most important reaction of N_2O was denoted as decomposition reaction, described as $2N_2O \leftrightarrow 2N_2 + O_2$.

In the low temperature range (usually 200–500 °C), precious metals, zeolite and transition metals (rhodium, *etc*.) all showed strong catalytic effect on N_2O decomposition [9,12]. N_2O decomposition rates reached 100% with $Rh/Na_2O/Al_2O_3$ as catalyst at a temperature of 425 °C. Besides, Fe-ZSM-5 or Co-ZSM-5 containing Co-, Cu-, Fe- or ZSM-5 were also beneficial to N_2O decomposition [10,11]. N_2O was decomposed on the surface of catalyst and the decomposition process could be described with following reactions [10]:

$$N_2O + * \rightarrow N_2 + O* \quad \text{(R-1)}$$

$$N_2O + O* \rightarrow N_2 + O_2 \quad \text{(R-2)}$$

In order to avoid catalyst destruction due to the fluctuation of N_2O concentration and reduce N_2O emission, reduction gases like H_2, CH_4 and CO were first used at the surface of catalyst [10,13,14]. Debbagh *et al*. [10] showed that N_2O decomposition with CO at catalyst surface at the temperature range of 200–600 °C was expressed with following reactions:

$$CO + O* \rightarrow CO_2 + * \quad \text{(R-3)}$$

$$CO + * \rightarrow CO* \quad \text{(R-4)}$$

$$N_2O + CO^* \rightarrow N_2 + CO_2 + ^* \quad \text{(R-5)}$$

Gluhoi *et al*. [13] studied the reactions of H_2 or CO with N_2O in the temperature range of 40–250 °C with the catalysts Au/TiO_2, Au/Al_2O_3, $Au/MIO_x/MIIO_x/Al_2O_3$, $Au/Mox/Al_2O_3$ (MI, MII, M = Li, Rb, Mg, Co, Mn, Ce, La, Ti), and proved that the presence of catalysts was beneficial for H_2, CO to reduce N_2O emissions. Kondratenko *et al*. [14] found that the reduction effect of CH_4 on N_2O was conspicuous with the catalytic effect of iron—silicalite at 450 °C, which could be expressed by the three following reactions:

$$N_2O + ^* \leftrightarrow N_2 + O^* \quad \text{(R-6)}$$

$$CH_4 + 3O^* \leftrightarrow CO + 2H_2O + 3^* \quad \text{(R-7)}$$

$$CH_4 + 4O^* \leftrightarrow CO_2 + 2H_2O + 4^* \quad \text{(R-8)}$$

Choosing the temperature range of 22–550 °C, with the effect of Fe-USY zeolite catalyst, and using selective catalytic reduction (SCR) method, Shen and co-workers [15] prepared a variety of mixed gases with CH_4 (such as N_2O/CH_4, $N_2O/CH_4/NO$, $N_2O/CH_4/O_2$, $N_2O/CH_4/H_2O$, $N_2O/CH_4/NO/O_2$, $N_2O/CH_4/NO/O_2/H_2O$) to study N_2O decomposition, concluding that N_2O conversion rate in N_2O/CH_4 system was much higher than that in other systems.

2. Experimental Devices and Method

The structure of the designed laboratory-scale fluidized bed reactor is shown in Figure 1. The reactor has an inner diameter of 15 mm and a height of 1900 mm and it contains an air distribution plate, vertically positioned in the electrical heating furnace. The bed material of the reactor consisted of screened ash and solid oxides ranging in diameter from 0.3 to 0.425 mm. In order to make the experimental circumstances more similar to the real conditions, circulating ash was used from a CFB power plant in Sichuan Province. Its composition is given in Table 1.

Figure 1. Schematic of the lab-scale quartz fluidized bed reactor.

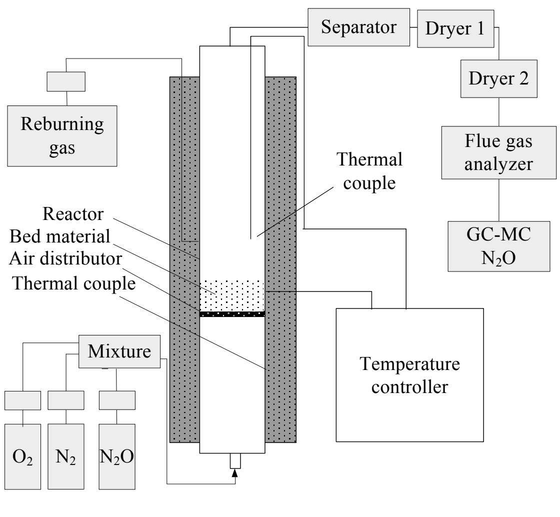


Table 1. Compositions of circulating ash from a CFB boiler (%).

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	TiO_2	$CaSO_4$	P_2O_5	K_2O	Na_2O
Circulating ash	33.22	13.91	6.66	11.59	1.59	1.97	31.88	0.18	1.01	0.30

Syngas (N_2/N_2O or $N_2/N_2O/O_2$) with 2000 ppm of N_2O was used as the flue gas and it was injected into the furnace from the bottom of the reactor with the flow rate 5000 mL/min. Another gas stream (H_2, CH_4 or CO) or syn-gas stream ($CH_4/CO/H_2/CO_2/N_2$ = 4.2/25.9/10.1/5.98/53.82) was used as the reburning gas and injected into the reactor from the side of the reactor, 200 mm above the air distribution plate, with flow rates ranging from 10 mL/min to 50 mL/min.

To discuss the mechanism of heterogenous N_2O decomposition with biomass gas and simulate a real CFB power plant, taking circulating ash as bed material in the CFB boiler, the influence of the main components of the biomass gas (H_2, CH_4 and CO) on heterogenous N_2O decomposition was analyzed. The oxygen contents in the flue gas were 0%, 2.5% and 6%. Reburning experiments were carried out by injecting biomass gas from a nozzle (with a distance of 0.2 m away from air distributor).

The exhaust gas was analyzed on-line by a flue gas analyzer (testo350Pro, Testo, Germany) to determine NO_2 and NO concentrations and collected for further analysis of N_2O content by gas chromatography (Trace DSQ, New York, USA) using a 3 m Porapark Q column. N_2O decomposition, and NO or NO_2 formation are calculated by the following equations:

$$\eta_{\mathrm{N_2O}} = \left(1 - \frac{\mathrm{N_2O}_{out}}{\mathrm{N_2O}_{in}}\right) \times 100\% \quad \text{(Eq-1)}$$

$$\eta_{\mathrm{NO}} = \frac{n_{\mathrm{NO},out}}{2n_{\mathrm{N_2O},in}} \times 100\% = \frac{[\mathrm{NO}]\cdot V_c}{22.4 \times 2n_{\mathrm{N_2O},in}} \times 100\% \quad \text{(Eq-2)}$$

$$\eta_{\mathrm{NO_2}} = \frac{n_{\mathrm{NO_2},out}}{2n_{\mathrm{N_2O},in}} \times 100\% = \frac{[\mathrm{NO_2}]\cdot V_c}{22.4 \times 2n_{\mathrm{N_2O},in}} \times 100\% \quad \text{(Eq-3)}$$

$$n_{\mathrm{N_2O},in} = \frac{Q_{\mathrm{N_2O}} \cdot \tau_c}{22.4} \quad \text{(Eq-4)}$$

where:

$n_{\mathrm{N_2O},out}$: mole of N_2O at the reactor outlet, mol;
$n_{\mathrm{N_2O},in}$: mole of N_2O at the reactor inlet, mol;
$n_{\mathrm{NO},out}$: mole of NO at the reactor outlet, mol;
$n_{\mathrm{NO_2},out}$: mole of NO_2 at the reactor outlet, mol;
$Q_{\mathrm{N_2O}}$: flow of N_2O inlet, mL/min;
τ_c: time of collecting gas in sample bag, min;
V_c: volume of collecting gas in sample bag, mL;
$[\mathrm{NO}]$: concentration of NO in exhaust gas, ppm;
$[\mathrm{NO_2}]$: concentration of NO in exhaust gas, ppm.

In research on the reburning character of biomass gasification gas, *R* represents the reburning gas content and can be calculated by:

$$R = V_b / V_f \times 100\% \quad \text{(Eq-5)}$$

where:

V_b: volume of biomass derived gas, mL;

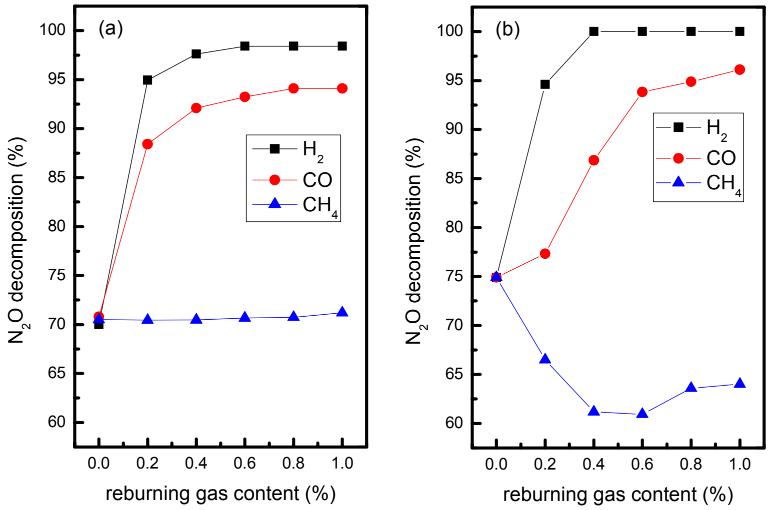
V_f: volume of flue gas, mL.

3. Results and Discussion

3.1. Influence of Biomass Gas Components without Oxygen in Flue Gas

Figure 2 shows that the N_2O decomposition rate changed with reburning gas content. Comparing the decomposition of N_2O before and after adding circulating ash as bed material, the thermal decomposition proportion of N_2O with bed material is about 5% larger than that seen with the bare bed conditions.

Figure 2. Relationship of N_2O decomposition and reburnig gas: (**a**) Homogeneous N_2O decomposition with bare bed; (**b**) Heterogeneous N_2O decomposition with circulating ash as bed material (N_2O = 2000 ppm, N_2O/N_2, 900 °C).



When H_2 is used as reburning gas, the conversion rate of N_2O decomposition with circulating ash is greater than that of the bare bed. When the CO content as reburning gas is less than 0.4%, N_2O decomposition rate with bed material is lower than N_2O that of the bare bed. This is because CO reacts with some components of the bed material, such as Fe_2O_3, which decreases the N_2O decomposition conversion. On the contrary, when the CO content as reburning gas is greater than 0.4%, the conversion of heterogenous decomposition will be higher than the conversion of homogenous decomposition. The effect of CH_4 as reburning gas on N_2O decomposition differs from that of H_2 and CO, as shown in Figure 2. The N_2O homogenous decomposition conversion part with CH_4 reburning was about 70%, but decreased sharply with circulating ash as bed material. However, when the content of CH_4 as reburning gas become greater than 0.6%, only a slight increase occurs. This is the result of the reactions of CH_4 and CaO in the circulating ashes [16]:

$$CaO + CH_4 \rightarrow CaOCH_4 \rightarrow CaOH + CH_3 \quad \text{(R-9)}$$

$$CaO + CH_4 \rightarrow OCaCH_4 \rightarrow HOCaCH_3 \rightarrow CaOH + CH_3 \quad \text{(R-10)}$$

$$CaO + CH_4 \rightarrow CaOCH_4 \rightarrow CaCH_3OH \rightarrow Ca + CH_3OH \quad \text{(R-11)}$$

$$CaO + CH_4 \rightarrow OCaCH_4 \rightarrow HCaOCH_3 \rightarrow CaOCH_3 + H \quad \text{(R-12)}$$

$$CaO + CH_4 \rightarrow OCaCH_4 \rightarrow CaCH_3OH \rightarrow CaOCH_3 + H \quad \text{(R-13)}$$

Corresponding to Figure 2, NO and NO_2 formation in the N_2O decomposition process are shown in Figures 3 and 4. When the reburning gas content is 0.2%, the NO formation reaches a maximum value. NO formation rate with H_2 as reburning gas is proven to be larger than that of CO and CH_4 with a bare bed. However, NO formation with CH_4 as reburning gas is more than CO and H_2 with circulating ash as the bed material.

Figure 3. Relationship of NO formation and reburning gas content: (**a**) Homogeneous N_2O decomposition; (**b**) Heterogeneous N_2O decomposition with circulating ash as bed material (N_2O = 2000 ppm, N_2O/N_2, 900 °C).

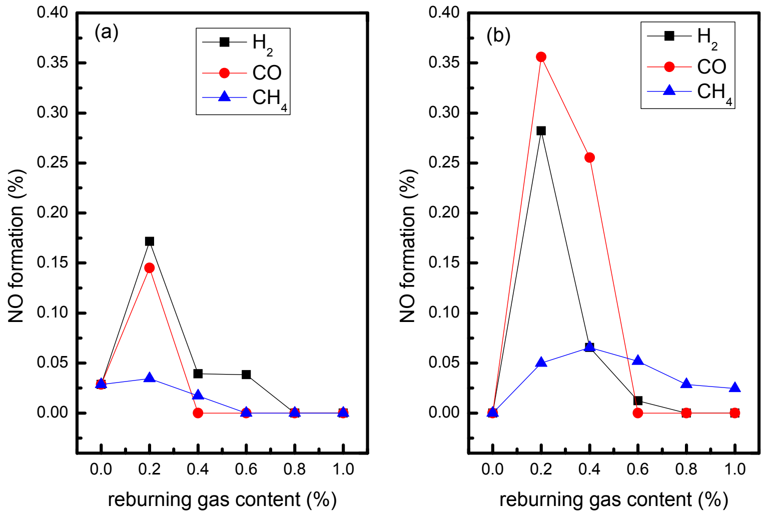
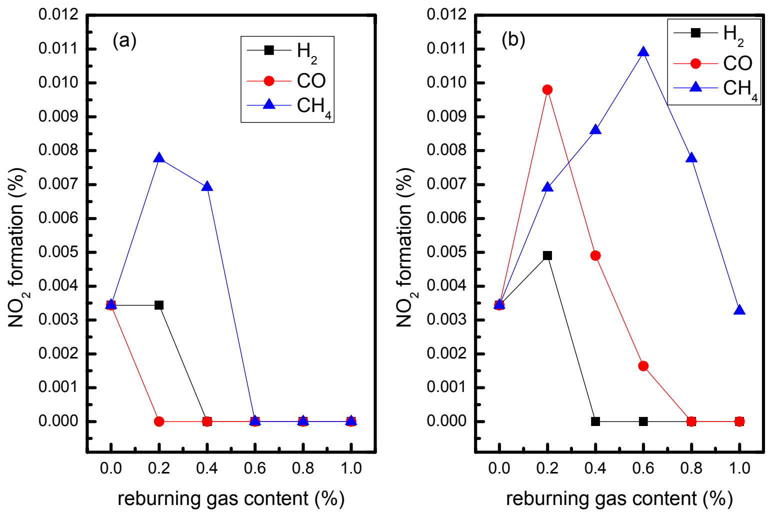


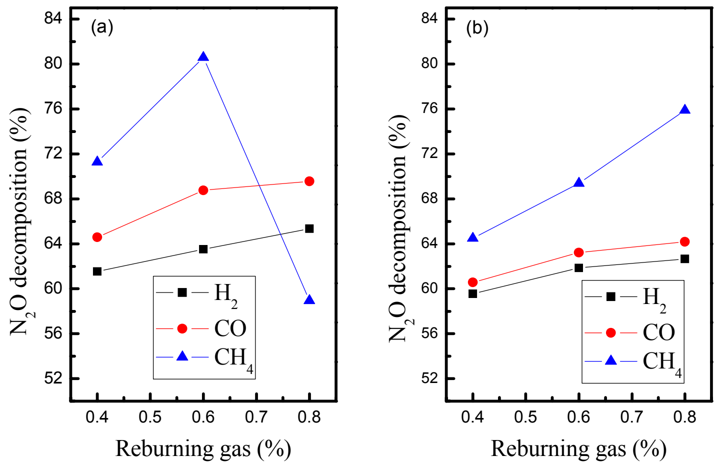
Figure 4. Relationship of NO_2 formation and reburning gas content: (**a**) Homogeneous N_2O decomposition; (**b**) Heterogeneous N_2O decomposition with circulating ash as bed material (N_2O = 2000 ppm, N_2O/N_2, 900 °C).



3.2. Influence of Biomass Gas Components with Oxygen Content in Flue Gas

The impacts of H_2, CH_4 and CO reburning gases on the rate of heterogenous N_2O decomposition conversion, depended on oxygen content, as shown in Figure 5. When the oxygen content in the flue gas is 2.5%, the N_2O conversion rate increases with the increase of H_2 and CO content (0.4–0.8 mole%), while the dependence of N_2O conversion on the CH_4 content achieves its maximum value at a CH_4 content of 0.6 mole%. However, when the oxygen content is 6%, it is very clear that N_2O conversion rises with increasing contents of H_2, CO and CH_4 in the reburning gas.

Figure 5. Relationship of heterogenous N_2O decomposition, reburning gas content and oxygen content in flue gas: (**a**) O_2 = 2.5%; (**b**) O_2 = 6% (N_2O = 2000 ppm, $N_2O/N_2/O_2$, 900 °C).



Figures 6 and 7 show NO formation and NO_2 formation in the N_2O conversion process (shown in Figure 5). With the circulating ash as bed material, NO and NO_2 formation at an oxygen content of 2.5% is higher than that under the condition of 6% oxygen content. The NO and NO_2 formation proportions with CO as reburning gas is more than that with CH_4 as reburning gas and it reaches its minimum value with H_2 as reburning gas.

Figure 6. Relationship of heterogenous NO formation, reburnig gas and oxygen content in flue gas: (**a**) O_2 = 2.5%; (**b**) O_2 = 6% (N_2O = 2000 ppm, $N_2O/N_2/O_2$, 900 °C).

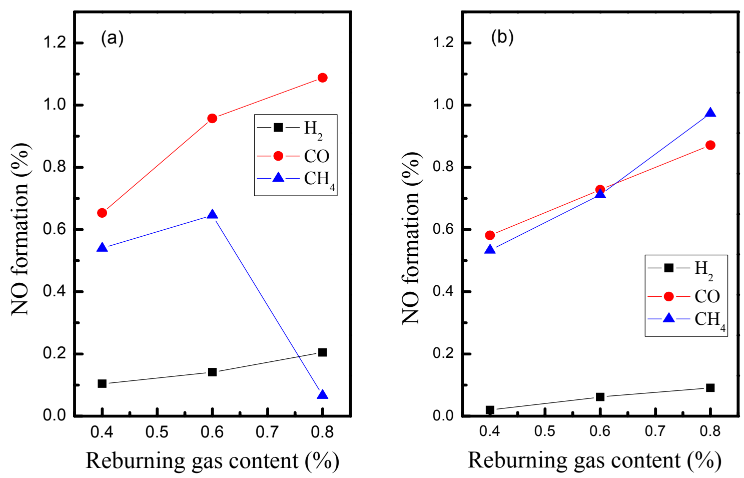
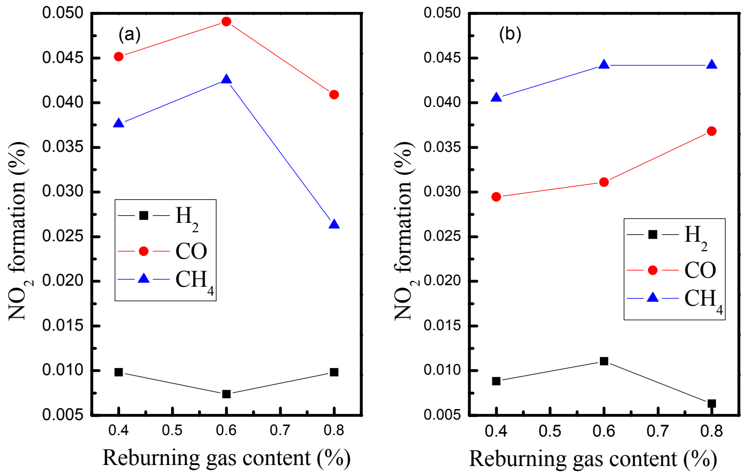


Figure 7. Relationship of heterogenous NO_2 formation, reburning gas and oxygen content in flue gas: (**a**) O_2 = 2.5%; (**b**) O_2 = 6% (N_2O = 2000 ppm, $N_2O/N_2/O_2$, 900 °C).



3.3. Influence of Ash and Metal Oxides on Heterogenous N_2O Decomposition

In order to analyze the catalytic effect of bed materials on N_2O decomposition, three sets of experimental conditions were compared, as shown in Figures 8–10. Thermal decomposition of N_2O with bed material and without biomass gas reburning is the first condition, in which the main conversion of N_2O is thermal decomposition. In the second conditions, considering the influence of biomass gas reburning, the heterogenous experiment was carried out without oxygen in the flue gas, a and a reductive condition was formed. Lastly, the catalytic effect of bed materials on N_2O decomposition is analyzed with biomass gas reburning and oxygen in the flue gas.

Figure 8. Influence of bed material on N_2O decomposition without biomass gas: (**a**) N_2O = 2000 ppm; (**b**) N_2O = 2800 ppm (with a height of bed material of 40 mm).

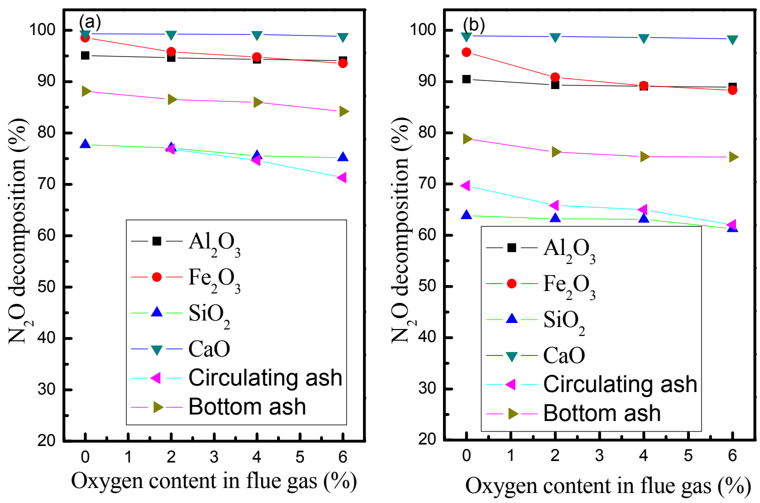


Figure 8 illustrates the order of the promoting effects of different bed materials on N_2O thermal decomposition without gas reburning. N_2O conversion rate is the highest when CaO is used as bed material at 900 °C. This indicates that CaO has the best promoting effect on N_2O conversion, playing the most significant role as catalyst and consistent with Barišić's research [17]. According to the study of a four type bed material from the bottom bed of two industrial CFB boilers, it is found that the combustion process of circulating fluidized bed boiler forms $CaSO_4$ with limestone consumption during the desulfurizing process. Barišić *et al*. proved that CaO is the most important component of bed material and the production of limestone with catalytic effect on N_2O conversion. In this paper, considering the promoting effect on N_2O conversion, CaO is followed by Fe_2O_3, Al_2O_3 and SiO_2.

The results show that N_2O conversion with CaO bed material and biomass gas reburning is the highest one among the three conditions (Figures 8–10). Therefore, given the fact limestone exists in actual CFB boilers as desulfurizer, its ejection together with biomass gas is the most effective way to reduce N_2O emissions.

Figure 9. Influence of biomass gas on heterogenous N_2O decomposition without oxygen content: (**a**) N_2O = 2000 ppm; (**b**) N_2O = 2800 ppm (with a height of bed material of 10 mm).

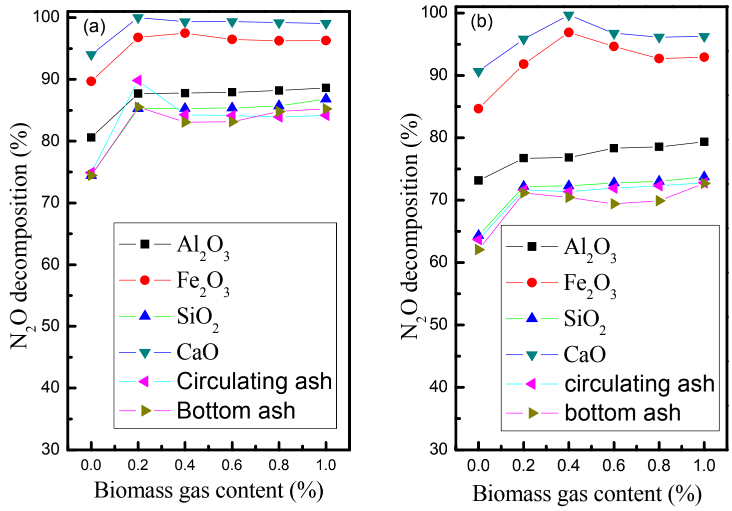
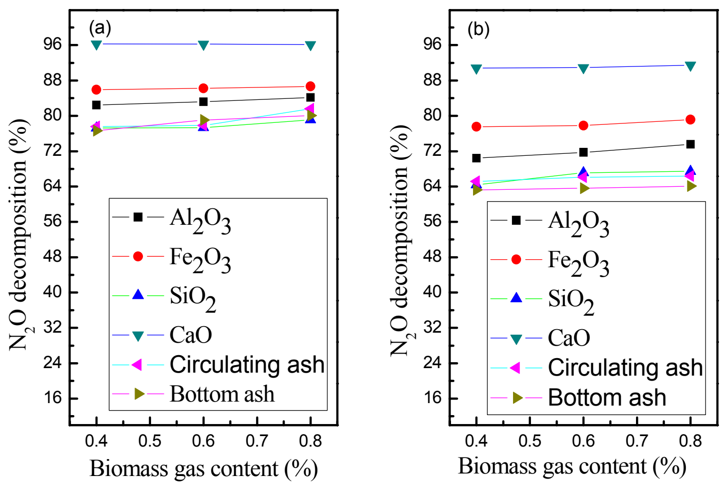


Figure 10. Influence of biomass gas on heterogenous N_2O decomposition with oxygen content was 5%: (**a**) N_2O = 2000 ppm; (**b**) N_2O = 2800 ppm (with a height of bed material of 10 mm).



4. Conclusions

Using a vertical fluidized bed reactor, reburning process with biomass gasification gas was investigated. Experiments of N_2O decomposition were carried out by changing the reburning gas and the bed material. It is concluded that:

(1) At the reaction temperature of 900 °C, the promoting effect order of CO, H_2 and CH_4 as biomass gas components on N_2O decomposition is: $H_2 > CO > CH_4$.
(2) Under the reductive conditions, the positive effect of H_2 is greater than that of CH_4 and CO on the conversion of heterogenous N_2O with the circulating ash as bed material, whereas under oxidative conditions with the same bed material, the impact of CH_4 is proven to be much stronger than that of H_2 or CO.
(3) With four different typical solid oxides and the circulating ash as bed material, the catalytic effect of CaO on the conversion of N_2O is more effective than that of Fe_2O_3, Al_2O_3 and SiO_2.

Acknowledgments

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