

## The effect of biomass pyrolysis gas reburning on N<sub>2</sub>O emission in a coal-fired fluidized bed boiler

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The fossil fuel consumption and pollutant emissions in a coal fired fluidized bed boiler could be reduced by biomass pyrolysis gas reburning. The influence of three kinds of biomass pyrolysis gases on the emission of N<sub>2</sub>O in a laboratory scale fluidized bed was investigated using the mechanism of GRI3.0 in this paper. The results showed that: the effect of sawdust pyrolysis gas reburning on N<sub>2</sub>O was more significant than that of rice husk and orange peel under the same conditions; the increase of initial oxygen content from 1% to 8% in flue gas would restrain the decomposition of N<sub>2</sub>O; the N<sub>2</sub>O decomposition was enhanced by increasing reaction temperature from 1073.15 K to 1323.15 K, and the decomposition rate may reach 99% at 1223.15 K.

**biomass pyrolysis gas, reburning, nitrous oxide (N<sub>2</sub>O), pollutant emission, fluidized bed**

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Biomass fuels is a form of renewable energy source, which can be considered CO<sub>2</sub> neutral fuels and giving lower emissions of SO<sub>2</sub>, NO<sub>x</sub>, and heavy metals respect to coals. NO<sub>x</sub> emissions could be reduced by using biomass, which contains low nitrogen and high volatile content [1–3]. As a normal power generation technology, biomass co-firing was initiated in Europe and the United States in the 1980s. Now there are more than 150 biomass co-firing power generation projects in the world [4,5]. This technique can reduce the emissions of NO<sub>x</sub> and CO<sub>2</sub> with lower fuel costs [6]. The typical biomass includes sawdust, agricultural wastes, animal wastes and anthropomorphic wastes. The most popular approaches to biomass utilization in electric power generation include [4,7–11]:

(1) Blending biomass with coal on the fuel pile: biomass and coal are mixed first, then milled and injected into the boiler combustor;

(2) Co-firing with separate injection: biomass and coal are mixed and burned in the boiler after being injected into the boiler separately;

(3) Gasification-based co-firing (also named reburning):

biomass is gasified first and then injected into the boiler for burning together with the waste gas produced from coal combusting.

Compared with indirect co-firing, there are some disadvantages for blending biomass with coal on the fuel pile and co-firing with separate injection [5,12]:

(1) With various shapes, biomass is difficult for fragmentation and may cause plugging in bunkers;

(2) Biomass contains high alkali metal and chlorine content, which may cause slagging and corrosion in coal-fired boilers with coal and have effect on the utilization of co-firing ash;

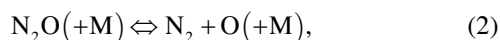
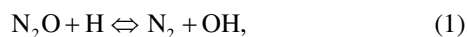
(3) Co-firing of biomass with coal may result in the deactivation of catalysts in denitration system.

In recent years, the large-scale coal-fired circulating fluidized bed (CFB) has been developed at a very fast pace with some problems correspondingly. As a greenhouse gas, N<sub>2</sub>O concentration produced in CFB is about 39 to 589 mg N<sup>-1</sup> m<sup>-3</sup>, sometimes as high as 786 mg N<sup>-1</sup> m<sup>-3</sup>, while it is generally less than 20 mg N<sup>-1</sup> m<sup>-3</sup> in traditional pulverized coal boiler [13,14]. The radial H produced in the process of fuel gas reburning has significant serious influence on N<sub>2</sub>O

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reduction [15]. The combustible material of biomass pyrolysis gas mainly contains  $H_2$ ,  $CH_4$  and  $CO$ , which are helpful to reduce nitrogen oxide emissions [5, 16, 17]. Because of low alkali metal and chlorine content, the gasified gas for co-firing can avoid most of the problems associated with direct co-firing, such as boiler fouling, corrosion and the utilization of co-firing ash. Therefore, reburning is considered as a promising technology. The effect on  $NO_x$  reduction depends on the type of fuel gases.  $CH_4$  and  $H_2$  are more effective than  $CO$ , which is enhanced by using catalysis and is influenced by the oxygen content in the flue gas [18–23]. The  $N_2O$  emission increases with the increase of excess air coefficient. The effect of strengthening air stage, the circulating material rate of quartz and coal particle was slight. The combustion of high rank coal produced more  $N_2O$  [16,13]. Besides, the  $N_2O$  emission was also influenced by the flow of fuel gases into the reactor and the feed point of coal [24].

In a small scale fluidized bed reactor, experiments of  $N_2O$  emission influenced by biomass pyrolysis gas reburning were carried out by Dong et al. [25,26]. The results showed that: the  $N_2O$  decomposition rate was improved by the increase of reburning temperature. With a biomass pyrolysis gas proportion of 1% and a reburning temperature of 1123.15 K, the rate was nearly 100%. The oxygen content of flue gas has a negative effect on  $N_2O$  decomposition, which is delayed by the increase of biomass pyrolysis gas. Based on the results above, the following reactions on  $N_2O$  reduction by reburning should be given more attention takes the most part in further research [27]:



In this paper,  $N_2O$  reduction is influenced obviously by the composition of biomass pyrolysis gas. With varied initial oxygen content, reaction temperature and the ratio of reburning fuel gases, sawdust, rice husk, and orange peel were chosen as the typical agricultural and forestry waste in this research.

## 1 Objectives and methodology

Reburning gas from sawdust, rice husk, and orange peel is produced by fast pyrolysis process at a temperature of 1123.15 K. Ultimate analysis, proximate analysis and pyrolysis gas components of them were given in [28].

The height of reactor was defined as the distance from the biomass pyrolysis gas inlet to the exhaust gas outlet, which is approximately 90 cm as shown in Figure 1. The construction of the model was based on the experimental part in literature [25,26]. In the chemical reaction process, the following assumptions have been made: (1) Biomass pyrolysis gas and flue gas were mixed perfectly before en-

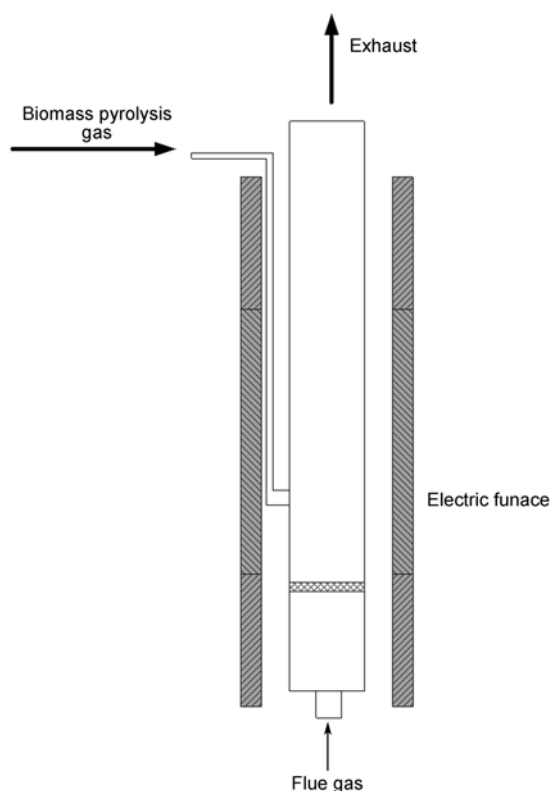


Figure 1 The schematic diagram of biomass pyrolysis gas reburning.

Table 1 Species in the model<sup>a)</sup>

Species in the model												
$H_2$	H	O	$O_2$	OH	$H_2O$	$HO_2$	$H_2O_2$	C	CH	$CH_2$	$CH_2(S)$	
$CH_3$	$CH_4$	CO	$CO_2$	HCO	$CH_2O$	$CH_2OH$	$CH_3O$	$CH_3OH$	$CH_2CO$	$CH_3CO$	$CH_2CO$	
$C_2H$	$C_2H_2$	$C_2H_3$	$C_2H_4$	$C_2H_5$	$C_2H_6$	HCCO	$CH_2CO$	$CH_3CO$	$CH_2CO$	$CH_3CO$	$CH_2CO$	
HCCOH	AR	N	NH	$NH_2$	$NH_3$	NNH	NO	$NO_2$	$N_2O$	$N_2O$	$N_2O$	
HNO	CN	HCN	$H_2CN$	HCNN	HCNO	HOCN	HNCO	HNCO	HNCO	HNCO	HNCO	
NCO	$N_2$	AR	$C_3H_7$	$C_3H_8$	$CH_2CHO$	$CH_3CHO$	$CH_3CHO$	$CH_3CHO$	$CH_3CHO$	$CH_3CHO$	$CH_3CHO$	

a) <http://www.me.berkeley.edu/gri-mech/version30/text30.html>.

tering the reaction tube; (2) the influence of mixing in the actual process was ignored; (3) The defined temperature at the inlet of the reactor was reached instantly, and the influence of temperature rise was ignored; (4) The plug flow model was used. The reaction mechanism was based on GRI3.0, which contains 325 chemical reactions and 53 species, whose detail information of species was given at Table 1.

The following equations of  $N_2O$  decomposition rate, NO formation rate and  $NO_2$  formation rate were chosen to evaluate  $N_2O$  reduction:

$$\eta_{N_2O} = \left( 1 - \frac{N_2O_{out}}{N_2O_{in}} \right) \times 100\%, \quad (4)$$

$$\eta_{NO} = \frac{NO_{out}}{2N_2O_{in}} \times 100\%, \quad (5)$$

$$\eta_{NO_2} = \frac{NO_{2out}}{2N_2O_{in}} \times 100\%, \quad (6)$$

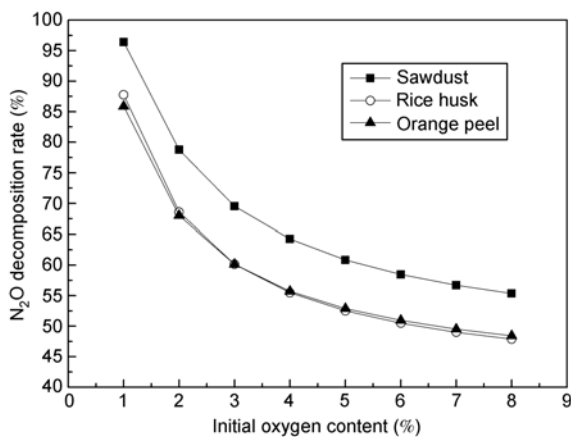
where  $N_2O_{in}$  and  $N_2O_{out}$  are the mole fraction of  $N_2O$  before and after the reaction respectively;  $NO_{out}$  and  $NO_{2out}$  are the mole fraction of  $NO$  and  $NO_2$  after the reaction respectively.

## 2 Results and discussion

### 2.1 The influence of initial oxygen content

Under the conditions of reaction temperature  $T=1173.15$  K,  $N_2O$  concentration  $c=2800$  ppm, residence time  $t=0.17$  s and the fraction content of biomass pyrolysis gas in flue gas  $R=1\%$ , and varied initial oxygen content, the comparison of the three kinds of biomass pyrolysis gas was shown in Figure 2. The results showed that the reduction effect of sawdust pyrolysis gas was better than that of orange peel and rice husk. The variation trend of different biomass pyrolysis gas influenced by initial oxygen content was consistent. When the initial oxygen content increased from 0 to 3%, the  $N_2O$  decomposition rate decreased quickly. With initial oxygen content was above 3%, the decomposition rate become insensitive. In the process of decomposition, the H radial was consumed during the biomass pyrolysis gas reburning process. With the increase of initial oxygen content, H radial reacts with O radial thus decrease the H radial concentration. On the other side, the reverse reaction of  $N_2O(+M) \rightleftharpoons N_2+O(+M)$  occurred with oxygen content increased. Additionally, the effect difference of the three kinds biomass pyrolysis gas on  $N_2O$  decreased at the same time [25]. Therefore, when biomass pyrolysis gas was used for reburning, higher  $N_2O$  decomposition rate could be achieved by choosing initial oxygen content less than 3%.

Using pyrolysis gas of sawdust, rice husk or orange peel, the influence trend of residence time on  $N_2O$  was similar. Take sawdust as an example, the effect of residence time and oxygen content on  $N_2O$  was shown in Figure 3. Keeping the oxygen content constant, the  $N_2O$  decomposition rate increased quickly when residence time varied from 0 s



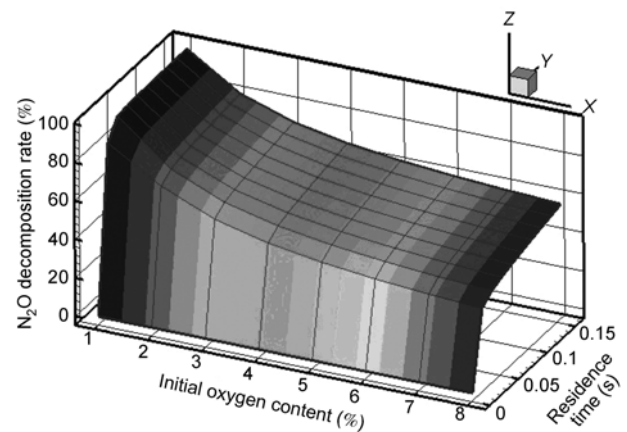
**Figure 2** The influence of oxygen content on  $N_2O$  decomposition ( $T=1173.15$  K,  $N_2O/O_2/N_2$ ,  $c_{N_2O}=2800$  ppm,  $t=0.17$  s,  $R_b=1.0\%$ ).

to 0.04 s; while it increased slowly when residence time was longer than 0.04 s. Because the residence time in CFB was more than 0.17 s, the  $N_2O$  decomposition rate increased slowly with residence time.

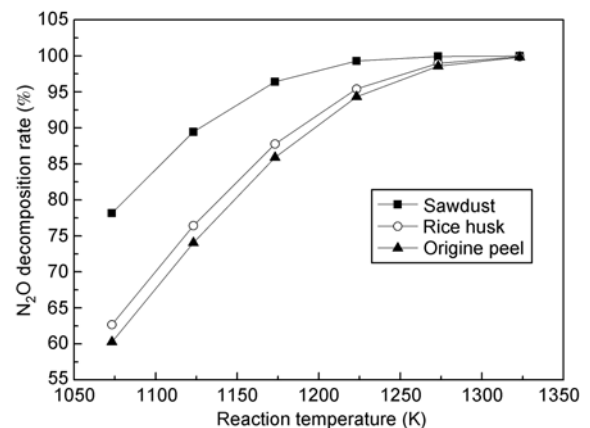
### 2.2 The influence of reaction temperature

As is shown in Figure 4, the  $N_2O$  decomposition rate increased along with bed temperature from 1073.15 K to 1323.15 K. With a reburning fuel ratio of 1.0% and a reaction temperature of 1223.15 K, the  $N_2O$  reduction remained unchanged, close to complete decomposition. With the change of temperature, the effect of sawdust on  $N_2O$  was better than that of rice husk and orange peel.

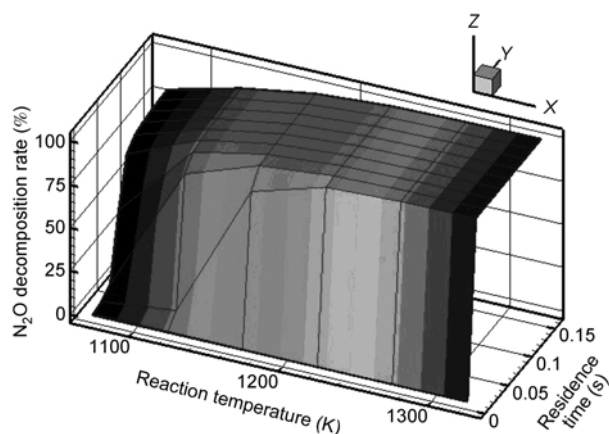
As is shown in Figure 5, with the increase of reaction temperature, the residence time of stable  $N_2O$  decomposition rates was shortened. When the temperature reaches 1273.15 K, the  $N_2O$  decomposition rate stayed 99% with a



**Figure 3** The influence of residence time and oxygen content of flue gas on  $N_2O$  decomposition rate (Sawdust,  $T=1173.15$  K,  $N_2O/O_2/N_2$ ,  $R_b=1.0\%$ ,  $c_{N_2O}=2800$  ppm).



**Figure 4** The influence of reburning fuels and reaction temperature on  $N_2O$  decomposition ( $N_2O/O_2/N_2$ ,  $R_{O_2}=1\%$ ,  $c_{N_2O}=2800$  ppm,  $t=0.17$  s,  $R_b=1.0\%$ ).



**Figure 5** The influence of residence time and reaction temperature on  $N_2O$  decomposition rate (Sawdust,  $N_2O/O_2/N_2$ ,  $R_{O_2}=1\%$ ,  $c_{N_2O}=2800$  ppm,  $R_b=1.0\%$ ).

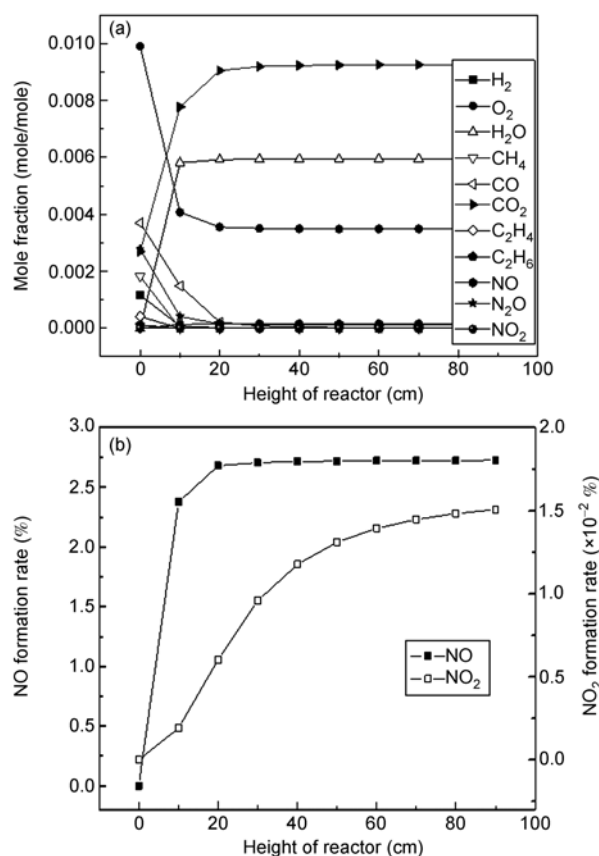
residence time of 0.02 s. The higher the reaction temperature, the more significant the reduction effect on  $N_2O$  emission, which was in good agreement with the conclusion in literature [25].

### 2.3 The influence of biomass gas content

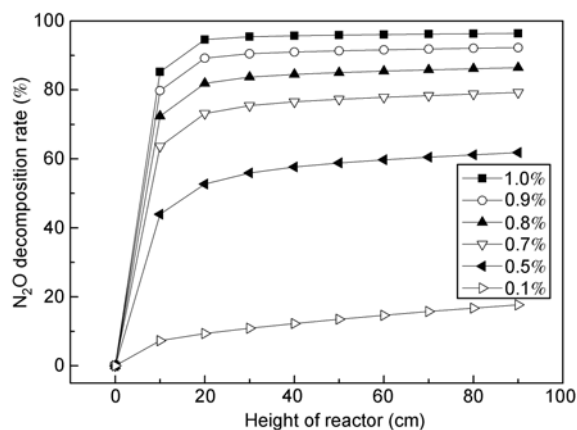
Using pyrolysis gas of sawdust, rice husk or orange peel, the influence trend of biomass pyrolysis gas content of flue gas on  $N_2O$  was the same. Taking sawdust for example, Figure 6 (a) showed the change of main species during  $N_2O$  reduction process at the temperature of 1173.15 K and the reburning fuel gas ratio of 1%. At the reactor exit,  $O_2$ ,  $H_2O$ ,  $CO_2$  and  $N_2$  were the main species, while the concentration of combustible gases  $H_2$ ,  $CH_4$ ,  $CO$ ,  $C_2H_4$ ,  $C_2H_6$ , and pollutants  $N_2O$ ,  $NO$  and  $NO_2$  were nearly zero.

All reactions mainly happened in the section of 0–20 cm, where various components of sawdust pyrolysis gas reacted with  $N_2O$ . In the process, the mole fractions of  $H_2O$  and  $CO_2$  were increased. Figure 6(b) indicated that most of  $N_2O$  was decomposed and converted into  $N_2$ , while only a small portion converted into  $NO$  and  $NO_2$ . Along with the reaction tube, the  $NO$  formation rate increased gradually and remained constant at 2.7%; while the increasing speed of  $NO_2$  formation rate slowed down with a value of 0.015% at the outlet of reactor. In a word, 1.35% of  $N_2O$  injected was converted into  $NO$  and 0.0075% was converted into  $NO_2$  under the operating conditions.

As is shown in Figure 7, with a certain reaction temperature,  $N_2O$  concentration and flue gas composition,  $N_2O$  decomposition rate was directly proportional to sawdust pyrolysis gas from 0.1% to 1%, especially at a distance of 0–20 cm. This was consistent with the conclusion in literature [25], where the  $N_2O$  decomposition rate increased with reburning fuel ratio from 0.4% to 1.4%.



**Figure 6** The mole fractions of main species(a) and the formation rate of  $NO$  and  $NO_2$  (b) in the reduction process of  $N_2O$  (Sawdust,  $T=1173.15$  K,  $N_2O/O_2/N_2$ ,  $R_{O_2}=1\%$ ,  $c_{N_2O}=2800$  ppm,  $R_b=1.0\%$ ,  $t=0.17$  s).



**Figure 7** The influence of different pyrolysis gas concentration on  $N_2O$  at different position of the reactor (Sawdust,  $T=1173.15$  K,  $N_2O/O_2/N_2$ ,  $R_{O_2}=1\%$ ,  $c_{N_2O}=2800$  ppm,  $t=0.17$  s).

## 3 Conclusions

Based on the studies about the influence of pyrolysis gas of sawdust, rice husk and orange peel on  $N_2O$  reduction under

CFB conditions, the following conclusions could be drawn:

(1) Under the same conditions, the reduction effect of sawdust pyrolysis gas on N<sub>2</sub>O was better than that of rice husk and orange peel;

(2) N<sub>2</sub>O decomposition was restrained by oxygen content when the flue gas increased from 1% to 8% and improved by the reaction when the temperature increased from 1073.15 K to 1273.15 K;

(3) With the increase of injected sawdust pyrolysis gas, N<sub>2</sub>O reduction rate was increased, among which 1.35% was converted into NO, while 0.0075% was converted into NO<sub>2</sub>.

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- 1 Zhang L H, Xu C, Champagne P. Overview of recent advances in thermo-chemical conversion of biomass. *Energ Convers Manage*, 2010, 51: 969–982
- 2 Fu P, Hu S, Sun L S, et al. Structural evolution of maize stalk/char particles during pyrolysis. *Bioresour Tech*, 2009, 100: 4877–4883
- 3 Daniele F, Riccardo C. CO<sub>2</sub> abatement by co-firing of natural gas and biomass-gasification gas in a gas turbine. *Energy*, 2007, 32: 549–567
- 4 Hu R Q, Qin S P, Fan J C. Policy research on biomass co-firing power generation (in Chinese). *Energ China*, 2008, 30: 22–25
- 5 Dong C Q, Yang Y P, Yang R, et al. Numerical modeling of the gasification based biomass co-firing in a 600 MW pulverized coal boiler. *Appl Energ*, 2010, 87: 2834–2838
- 6 McIlveen Wright D R, Huang Y, Rezvani S, et al. A technical and environmental analysis of co-combustion of coal and biomass in fluidised bed technologies. *Fuel*, 2007, 86: 2032–2042
- 7 Tillman D A. Biomass cofiring: The technology, the experience, the combustion consequences. *Biomass Bioenerg*, 2000, 19: 365–384
- 8 Brouwer J, Owen W D, Harding N S, et al. Cofiring waste biofuels and coal for emissions reduction. *Prepr Pap Am Chem Soc Div Fuel Chem*, 1995, 40: 66–71
- 9 Swanekamp R. Biomass co-firing technology debuts in recent test burn. *Power*, 1995, 139: 51–53
- 10 Hunt E F, Prinzing D E, Battista J J, et al. The Shawville coal/biomass cofiring test a coal/power industry cooperative test of direct fossil-fuel CO<sub>2</sub> mitigation. *Energ Convers Manage*, 1997, 38: 551–556
- 11 Surmen Y, Demirbas A. Cofiring of biomass and lignite blends: Resource facilities, technological and environment issues. *Energ Sourc*, 2003, 25: 175–187
- 12 Khan A A, De Jong W, Jansens P J, et al. Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Process Technol*, 2009, 90: 21–50
- 13 Xie J J, Yang X M, Zhang L, et al. Emissions of SO<sub>2</sub>, NO and N<sub>2</sub>O in a circulating fluidized bed combustor during co-firing coal and biomass. *J Environ Sci-China*, 2007, 19: 109–117
- 14 Armesto L, Boerrigter H, Bahillo A. N<sub>2</sub>O emissions from fluidized bed combustion: The effect of fuel characteristics and operating conditions. *Fuel*, 2003, 82: 1845–1850
- 15 Gustavsson L, Glarborg P, Leckner B. Modeling of chemical reactions in afterburning for reduction of N<sub>2</sub>O. *Combust Flame*, 1996, 106: 345–358
- 16 Duan J, Luo Y H, Yan N Q, et al. Experimental study on the characteristics of biomass gasification-reburning (in Chinese). *J Fuel Chem Tech*, 2007, 35: 245–248
- 17 Lissianski V, Zamansky V, Rizeq G. Integration of direct combustion with gasification for reduction of NO<sub>x</sub> emissions. *P Combust Inst*, 2002, 29: 2251–2258
- 18 Rutar T, Kramlich J C. Nitrous oxide emission control by re-burning. *Combust Flame*, 1996, 107: 453–463
- 19 Vandoooren J, Van Tiggelen P J. Experimental and modeling studies of a rich H<sub>2</sub>/CO/N<sub>2</sub>O/Ar flame. *Combust Flame*, 1997, 109: 647–668
- 20 Gluhoi A C, Dekkers M A P, Nieuwenhuys B E. Comparative studies of the N<sub>2</sub>O/H<sub>2</sub>, N<sub>2</sub>O/CO, H<sub>2</sub>/O<sub>2</sub> and CO/O<sub>2</sub> reactions on supported gold catalysts: Effect of the addition of various oxides. *J Catal*, 2003, 219: 197–205
- 21 Kosarev I N, Starikovskaia S M, Starikovskii A Y. The kinetics of auto-ignition of rich N<sub>2</sub>O–H<sub>2</sub>–O<sub>2</sub>–Ar mixtures at high temperatures. *Combust Flame*, 2007, 151: 61–73
- 22 Kondratenko E V, Pérez Ramírez J. Mechanistic peculiarities of the N<sub>2</sub>O reduction by CH<sub>4</sub> over Fe-silicalite. *Catal Today*, 2007, 119: 243–246
- 23 Dong C Q, Yang Y P, Zhang J J, et al. Gaseous emissions from the combustion of a waste mixture containing a high concentration of N<sub>2</sub>O. *Waste Manage*, 2009, 29: 272–276
- 24 Yoshizo S, Hiroshi M. Reduction of N<sub>2</sub>O emissions from circulating fluidized bed combustors by injection of fuel gases and changing of coal feed point. *Energ Convers Manage*, 1996, 37: 1285–1290
- 25 Dong C Q, Hu X Y, Li Y S, et al. Product gas combustion in fluidized bed for N<sub>2</sub>O reduction. In: *International Conference on Sustainable Power Generation and Supply*, April 6–7 2009, Nanjing. Piscataway: IEEE Service Center, 2009. 1–7
- 26 Li Y S. The Influence of Biomass Gas Burning in Fluidized Bed on N<sub>2</sub>O Emission (in Chinese). Master Dissertation. Beijing: North China Electric Power University, 2009
- 27 Hu X Y, Dong C Q, Yang Y P, et al. Mechanism Study on N<sub>2</sub>O Reduced with Biomass Gas. In: *Guerrero J E, ed. International Conference on Environmental Science and Information Application Technology*, July 4–5 2009, Wuhan. Piscataway: IEEE Service Center, 2009. 52–56
- 28 Li G, Chi Z H, Si D P. Test and study on reburning of biological wastes to reduce NO<sub>x</sub> emission (in Chinese). *Therm Pow Gen*, 2004, 33: 41–44

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