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An experimental study of NO reduction by biomass reburning and the characterization of its pyrolysis gases

Yun Shu, Fan Zhang [*], Hongchang Wang, Jinwei Zhu, Gang Tian, Chen Zhang, Yutao Cui, Jiayu Huang

Research Center of Air Pollution Control Technology, Chinese Research Academy of Environmental Sciences, Beijing 100012, China

HIGHLIGHTS

- Biomass type had a significant influence on NO reduction efficiency.
- Difference in NO reduction was due to difference in yield of pyrolysis gas of biomass.
- Hydrocarbons (mainly CH_4) were mainly responsible for NO reduction.

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ABSTRACT

The reduction of NO by reburning using three biomass samples (rice husk, sawdust and corncob) was investigated in a horizontal fixed-bed quartz reactor. The temperatures were ranging from 800 to 1200 °C. The influence of the oxygen concentration entering the reburning zone, the particle size of the biomass and the initial NO concentration on the NO reduction efficiency were studied experimentally. In order to improve the understanding of the relative contribution of each of the pyrolysis gases on the NO reduction, the CO, H_2, hydrocarbons (mainly CH_4), HCN, and NH_3 concentrations in the outlet gas from the reburning zone were measured at combustion temperatures of 800–1200 °C. The experimental results indicated that the biomass type had a significant influence on the NO reduction efficiency. The maximum NO reduction efficiency of sawdust reburning ($55 \pm 2.4\%$) was much higher than those of rice husk reburning ($43 \pm 1.8\%$) and corncob reburning ($44 \pm 2.1\%$). For reburning with sawdust, a highly efficient NO reduction was achieved at oxygen inlet concentrations of 0–1 vol%, particle sizes of 160–370 μm and initial NO concentration of 800 ppmv. For the present operating conditions, the difference in NO reduction for the three biomass samples could be ascribed to differences in the yield of pyrolysis gases through the homogeneous reactions. Hydrocarbons (mainly CH_4) were the key species for reducing the emissions of NO, whereas CO and H_2 had little effect on NO reduction. The sum of the HCN and NH_3 concentrations could reflect the tendency for the conversion of the NO entering the reburning zone into N_2.

1. Introduction

Nitric oxides (mainly NO) are one of the main air pollutants emitted from coal-fired boilers. They can cause a variety of environmentally harmful effects such as acid rain, ozone depletion and urban smog. In recent years, various technological approaches have been used to reduce the nitric oxides emissions from combustion systems [1–3]. Reburning is recognized as one of the most promising combustion modification technologies for NO control. In the reburning process, a secondary fuel is injected downstream from the main combustion region, to generate a fuel-rich reburn zone inside a furnace, where hydrocarbon radicals and heterogeneous reactions promote the reduction of NO formed in the main combustion region to N_2. To complete the process, over-fire air is introduced prior to the furnace exit to oxidize carbon monoxide, hydrogen, and any remaining combustible compounds exiting the reburning zone [4–6].

Many types of fuel have been investigated as reburning fuels, including natural gas [7], coal [8] and biomass [9,10]. Compared with other fuels, biomass as a reburning fuel has several advantages [11–14]: (1) biomass fuels contain lower levels of sulfur and nitrogen, suggesting their lower SO_2 and NO_x emissions, (2) they are renewable and nearly CO_2-neutral fuels, and (3) they have a higher content of volatile matter, leading to a greater reduction of NO_x.

It is well known that NO reduction reactions with solid fuels include homogeneous reactions between NO and volatiles and heterogeneous reactions between NO and chars. Wendt [15] and

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[*] Corresponding author. Tel.: +86 10 84915188; fax: +86 10 84934516.
E-mail address: zhangfan5188@vip.sina.com (F. Zhang).

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Mereb [16] hypothesized that the heterogeneous reactions contributed to low levels of NO reduction during the reburning process. The reduction potential of a fuel depended on its ability to produce volatiles that react with NO. Assuming that only homogeneous gas-phase reactions participated in the reduction, the fuel with a higher volatile matter content would be expected to achieve a greater NO reduction. Cancès et al. [17] also reported that homogeneous reduction was the most efficient mechanism for reburning process. Furthermore, some researchers thought that the good reburning performance of biofuels could be explained by their high volatiles yields (mainly hydrocarbon), similarly to the mechanism of natural gas reburning [18]. In addition, the other pyrolysis gases, CO, H_2 and some nitrogen-containing species (HCN and NH_3), also play an important role in NO reduction [19,20]. Indeed, the pyrolysis gas from biomass has been shown to reduce NO effectively, and different pyrolysis gases have different NO reduction potentials. Thus, it is thought that biofuels with different compositions under the pyrolysis conditions in the reburning zone will be expected to produce different pyrolysis gases that, in turn, can radically change the NO reburning effectiveness. However, taking into account existing studies in the literature, a detailed characterization of the pyrolysis gases in the biomass reburning process is absent. Better knowledge of the relative contribution of each of the pyrolysis gas species to NO reduction is required.

In the present work, the NO reduction performances of different biomass samples as reburning fuels (rice husk, sawdust and corncob) were evaluated. The effects of crucial parameters, such as the oxygen concentration entering the reburning zone, the particle sizes of the biomass and the initial NO concentration, on the reburning process were analyzed. In the temperature range of 800–1200 °C, much attention was paid to the detailed characterization of the distribution of the key pyrolysis gaseous species (CO, H_2, hydrocarbons (mainly CH_4), HCN and NH_3) for the three biomass samples during the reburning process.

2. Experimental

2.1. Samples

Three different biomass samples, namely rice husk, sawdust, and corncob, were used in this study. All of the biomass samples were ground and sieved to a size range of 160–370 μm before analysis and use in the experiments. The proximate and ultimate analyses of the biomass samples are shown in Table 1, according to the test standard of coal. The composition of pyrolysis products collected by biomass is shown in a weight ratio (wt%) in Table 1. As shown in the table, the biomass samples showed high volatile matter and low N and S contents, and their heating value was in the range from 15.06 to 17.53 MJ/kg. These values indicated that the samples were ideal renewable energy resources with minor potential for environmental pollution. The ash analysis of the biomass samples was performed using X-ray fluorescence spectroscopy (XRF) (results shown in Table S1). These results were reported on an oxide basis as a percentage of the ash mass. The main inorganic elements in the biomass samples were Na, K, Si, etc. The results showed that sawdust had the highest amount of Na_2O, whereas rice husk had the highest amount of SiO_2, and corncob showed the highest K_2O.

Table 1
Characteristics of biomass samples.

Samples	Rice husk	Sawdust	Corncob
Proximate analysis (wt%, as air dried)			
Moisture	4.01	3.34	4.65
Ash	15.48	2.98	5.26
Volatile matter	64.43	74.38	72.09
Fixed carbon	16.08	19.30	18.00
Ultimate analysis (wt%, as air dried)			
C	39.47	45.56	43.70
H	4.85	5.57	5.27
O	35.02	38.59	39.67
N	0.48	1.28	0.54
S	0.04	0.03	0.06
LHV (MJ/kg)	15.06	17.53	16.38

2.2. Experimental system and procedures

The experimental setup was composed of a reaction system, a gas feed system and a continuous analysis system, as illustrated in Fig. 1.

An annular electric furnace with a temperature control unit was used to simulate the reaction conditions in the reburning zone. A Pt-Rh thermocouple measured the temperature in the electric furnace, and the precision of the temperature control was ±1 K. The reburning experiments were performed in a horizontal fixed-bed quartz reactor with a length of 1200 mm and an inner diameter of 60 mm. The reactor was heated by the electric furnace. The reactor could withstand temperatures as high as 1250 °C, and the heated zone was 800 mm in length. The reaction temperature in the reburning zone was controlled in the range of 800 to 1200 °C. An example of the temperature profile obtained for different system temperatures is shown in Fig. 2. As shown, the shape of the temperature profiles was very similar for all of the system temperatures. There was a central zone (approximately 500 mm in length) where the temperature could be considered fairly uniform. In the gas feed system, the high-purity N_2, CO_2, O_2, and 2 vol% NO with N_2 gases from different gas cylinders first passed through the mass flow controllers before entering a mixing chamber, where the different gases were mixed prior to being fed into the horizontal quartz reactor as the simulated flue gas. Water vapor was generated by passing N_2 through a heated gas-wash bottle containing deionized water. The volume fractions of CO_2, O_2, NO and H_2O in the simulated flue gas were 15 vol%, 0–4 vol% (when used), 200–1200 ppmv (when used) and 6 vol%, respectively, and these concentrations were chosen according to measurements at the exit of the primary zone of a coal-fired boiler. The balance gas was N_2. The flue gas residence time in the reburning zone was estimated to be approximately 600 ms, corresponding to total flue flow rates between 1500 and 2000 NL/h (corresponding to 101,325 Pa and 0 °C on a dry basis) for reaction temperatures between 800 and 1200 °C. The typical reburning zone parameters are shown in Table 2. The reburning experiments were performed under atmospheric pressure. Before each experiment, a ceramic boat containing the biomass sample (approximately 2 g) was placed in the cold side of the reactor. Then, the reactant gases were flowed through the reactor, which was already preheated to the desired temperature, to measure the gas compositions. The biomass sample with a ceramic boat was then rapidly introduced into the reactor by a push–pull rod to start the reburning experiment after the detected concentrations of the reactant gases were stable. The biomass samples combusted, and the volatiles emitted from biomass could react with the flue gas to accomplish the reburning process.

The concentrations of CO, NO, CH_4, HCN and NH_3 in the outlet gas from the reburning zone were continually measured by a Fourier transform infrared (FTIR) analyzer system (GASMET DX-4000), produced by Gasmet Technologies, Inc. in Finland. The O_2 and NO concentrations were measured using an electrochemical gas analyser (Testo 340), and the concentrations of hydrocarbons (CH_4, C_2H_2, C_2H_4 and C_2H_6) and hydrogen were measured by gas chromatography (Agilent Technologies, 3000 Micro GC) with a flame ionization detector (FID) and a thermal conductivity detector