Atmospheric Environment 132 (2016) 290–295

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Technical note

Influence of the biogas reburning for reducing nitric oxide emissions in an alundum-tube reactor

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HIGHLIGHTS

- Biogas reburning could effectively reduce NO emissions.
- The foremost component in NO-reduction by biogas reburning was CH_4.
- Under a low λ, H_2 could enhance the concentration of CH_3 radicals, thereby increasing the reduction efficiency of NO.
- NO-reduction by CO in biogas reburning was negligible.

ARTICLE INFO

Article history:
Received 1 December 2015
Received in revised form
22 February 2016
Accepted 2 March 2016
Available online 4 March 2016

Keywords:
Atmospheric pollutants
NO
Biogas
Reburning
Reduction efficiency

ABSTRACT

The experimental study on reburning reduction reaction between biogas and NO is very important in de-NO_x technology. The reburning experiments by the simulated biogas with different operation variables have been performed in an alundum-tube reactor. Results showed that the uppermost constituent in NO-reduction was CH_4, H_2 second, and NO-reduction by CO in biogas reburning was negligible at the same conditions. In the condition of oxygen-poor, H_2 could promote CH_4 oxidation and enhance the concentration of CH_3 radicals, thereby increasing the reduction efficiency of NO accordingly. At the same temperature, with the increase of stoichiometric ratio, it would increase O radicals and decrease NO reduction efficiency. With the increase of reaction temperature, the reduction efficiency behaved a trend of first increased then decreased at the same stoichiometric ratio, and obtained the maximum value 51.38% at the condition of 1200 °C and $\lambda = 0.6$. Additionally, increasing the NO input concentration also could improve the reduction efficiency under the condition of fuel-rich.

1. Introduction

Nitrogen oxides (primarily NO, 90–95%) are one of the most serious atmospheric pollutants emitted from coal-burning boilers and kilns, which will cause acid rain, acid mist and even photochemical smog (Shu et al., 2015a,b; Zhao et al., 2015; Liu et al., 2015a,b). More than that, it not only causes a serious threat to the sustainable development of ecological environment, but also can harm people's health and lower their quality of life. With the development of human society and the advancement of civilization, people have attached more importance to environmental pollution problems. Therefore, how to reduce NO_x emissions has become more and more urgent and important. Among reburning is regarded as one of the most promising cleaner control and cost-efficient NO_x reduction technology for coal burning systems (Smoot et al., 1998; Su et al., 2009).

In recent years, a number of scholars want to improve the denitration efficiency through seeking optimal reburning fuels, including superfine pulverized coal (Hampartsoumian et al., 2003; Luan et al., 2009; Liu et al., 1997, 2015a,b), natural gas (Giménez-López et al., 2011; Casaca and Costa, 2011; Su et al., 2009; Bilbao et al., 1995), biomass (Cancès et al., 2008; Harding and Adams, 2000; Su et al., 2010; Shu et al., 2015a,b; Ballester et al., 2008) and biogas (Wu et al., 2015; Glarborg et al., 2000; Dagaut and Lecomte, 2003; Pisupati and Bhalla, 2008; Fan et al., 2006). Biomass as reburning fuel has remarkable NO_x reduction effect (Casaca and Costa, 2005, 2009), but it will generate a great quantity of tar which will damage the combustion equipment. Compared with other reburning fuels, biogas has its own unique advantages:

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http://dx.doi.org/10.1016/j.atmosenv.2016.03.004
1352-2310/

(1) it does not contain ash content, suggesting its lower corrosion; (2) it has null or minimal content of nitrogen; (3) it generates hydrocarbon radicals more easily which make the reduction reaction between biogas and NO more actively.

Biogas as reburning fuels, not only can realize the comprehensive utilization of agriculture and forestry waste and other biomass energy, but also can correspondingly reduce the total weight of coal-burning in coal-fired boilers and kilns. Combining the national condition of China, it is not difficult to find that the biogas as reburning fuels will have very extensive application prospect in the future. Over the past decade, a number of experiments and investigations about biogas reburning have been performed. Thereinto, Dagaut and Lecomte. (2003) studied the reduction of NO by simulated biomass pyrolysis gases reburning ($CO/H_2/CH_4/C_2H_4/C_2H_2$) in a fused silica jet-stirred reactor, the results showed that the higher temperature and moderate fuel-rich conditions were beneficial for NO-reduction, and it also revealed the reaction mechanism of NO-reduction with simulated biomass pyrolysis gases reburning. Pisupati and Bhalla (2008) through the experiment to verify the simulation results on the reduction of NO by using biomass pyrolysis gas as reducing agent in a sedimentation furnace, the results displayed that CO, H_2 and CO_2 had negligible impact on the reduction of NO, and hydrocarbons were the foremost component which were used to reduce the NO emissions. Fan et al. (2006) studied the reduction emission of NO by the reburning reduction reaction between simulating biogas and simulated flue gas, the results showed that the biogas could effectively reduce the emissions of NO, and increasing the reburning zone reaction temperature could effectively promote the NO-reduction.

The interaction functional mechanism of each constituent in biogas reburning was very complex, and the different constituents would result in great differences in NO-reduction. Different from other researches, this note not only studied the impact of stoichiometric ratio, reburning reaction temperature and the NO input concentration, but also discussed the reducibility of CO, H_2 and CH_4.

2. Experimental procedure and methods

2.1. Experimental procedure

The simulated biogas reburning experiments were performed in a self-designed testing device, which consisted of an electric heating system, a vertical tube reactor system, a temperature controlling and monitoring system, a simulated biogas feeding system, a simulating flue gas feeding system and a flue gas inspecting and analysis system, as shown in Fig. 1.

The reactor system is composed of ambient refractory and a cylinderical alundum-tube whose inner diameter is 60 mm and total length was 720 mm, and electrically heated. The total power of this electric heating furnace is 6 kWth, and the reactor is heated by ambient heating elements of silicon carbide. Through the temperature control unit, the vertical alundum-tube reactor is divided into three different temperature region, among the temperature of reburning zone can keep isothermal and even the maximum temperature can reach up to 1500 °C. Thereinto, the total length of reburning reaction zone is decided by the lifter equipment and multihole ejector, whose detailed structure chart is presented in the Supplementary Material. In addition, the temperature of furnace chamber is measured by Pt-Rh thermo-couple, which can effectively measure the temperature of reaction chamber with the precision of ±2 °**C**. In order to avoid the heat dissipation outward from the combustion chamber, the asbestos were used to block the clearances.

The reburning reaction temperature can be controlled in the region of 900–1400 °C via adjusting the temperature controller, in other words, the reburning reduction reactions will happen at isothermal conditions so that it can get better results for removing NO. In the simulated biogas and flue gas feeding system, the high purity N_2, O_2, H_2, CH_4, CO, CO_2 and 0.68 vol% NO with N_2 from various high-pressure gas cylinders first went through the volumetric flowmeters prior to entering the mixer, then the various kinds of gas were mixed enough before being injected into the vertical alundum tube reactor as the reactant gases. Water vapor can be generated by the atomizer (KingZone, CN), and then entrained by N_2 into the reburning zone.

Before recording the experimental data, we should guarantee that the simulated biogas and simulating flue gas can be mixed adequately. Moreover, N_2 was used to purge the furnace chamber before each experiment. In order to guarantee the accuracy of experimental results, the repeated tests were performed at least three times.

2.2. Analytical methods

The concentrations of CO, H_2, CH_4 and NO can be measured and analyzed by hand-held gas analyzer (E4400-S, USA) and gas chromatograph-mass spectrometer (GC6890-5973MS, USA). Thereinto, the volume fraction of input gas can be measured by E4400-S analyzer equipped with longer probe in initial mixing zone. The component proportion of biogas can be controlled by adjusting the flow rate of CO, H_2, CH_4, CO_2 and N_2 (balance carrier gas), respectively.

In this note, the stoichiometric ratio can be defined as:

$$\lambda = \frac{V_{O_2}}{2V_{CH_4} + 0.5V_{H_2} + 0.5V_{CO}}$$

where V_{O2}, V_{CH4}, V_{H2} and V_{CO} are the O_2, CH_4, H_2 and CO input volume fractions in reburning zone, respectively.

The reduction efficiency of NO can be defined as:

$$\eta_{NO} = \frac{[NO]_{j,inlet} - [NO]_{j,outlet}}{[NO]_{j,inlet}} \times 100\%$$

where η_{NO} is the transient NO reduction efficiency, %; $[NO]_{input}$ is the NO initial input concentration in reburning zone, ppmv; $[NO]_{outlet}$ is the NO outlet concentration, ppmv; j denotes the CH_4, H_2, CO or simulated biogas. Repeatability of the NO measured data was, on average, within 5%.

3. Results and discussion

3.1. Effects of $CH_4/H_2/CO$ on NO-reduction

Fig. 2 shows the experimental and calculated effects of NO reduction efficiency with distinct CH_4 input volume fractions ($\lambda = 0.6$). It could be seen that the input volume fractions of CH_4 played a significant influence on NO-reduction, and the largest reduction efficiency all exceed 50% ranging from 1200 °C to 1400 °C. However, CH_4 presented a lower reduction effect at 900 °C, and that only coupled with slight change. With the increase of input volume fraction, the NO reduction efficiency also increased gradually at the same reburning temperature. Moreover, the reduction efficiency obtained an optimal value at 1200 °C and maximal CH_4 input volume fractions.

Different from light hydrocarbons, H_2 presented a much lower reducibility on the reduction of NO. As presented in Fig. 3, the ability of H_2 to reduce NO emissions was quite weak at 900 °C. With the increase of H_2 input concentration, the NO reduction efficiency also increased accordingly with smaller and smaller increment rate.