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NO and N₂O Emission Characteristics from a Pilot Scale Vortexing Fluidized Bed Combustor Firing Different Fuels

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This study investigated experimentally the effects of various operating conditions, such as bed temperature, excess air, fuel property, and the method of temperature control on NO and N₂O emissions. All the experiments are conducted in a pilot scale vortexing fluidized bed combustor (VFBC). The cross section of the combustion chamber is 0.64×0.32 m², and the inner diameter of the freeboard is 0.45 m. Rice husk, soybean, and high sulfur subbituminous coal are used as fuels. Silica sand is employed as the bed material. The experimental results reveal that NO emissions increase with excess air and are almost independent of the bed temperature (600–760 °C). In addition, the amount of NO and N₂O increases while water is injected into the combustor. The high-volatile fuel appears to form a significant amount of NO and N₂O above the bed surface. However, NO emission detected at the outlet of the combustor decreases with the volatile content. Compared with the primary air, the bed temperature is the dominant factor for the trade off NO and N₂O. Most of the NO is formed above the bed surface, achieves a maximum value at the position below the inlet of second air, and is reduced considerably within the freeboard. Moreover, the most remarkable feature about them is that N₂O emission from combustion can be neglected no matter what the feeding material is.

1. Introduction

Compared with other combustors, lower NO emissions can be achieved by employing the fluidized bed combustor (FBC). This can be attributed to the lower operating temperature which prevents the formation of the thermal NO and prompt NO during the combustion process. On the other hand, biomass and biomass-derived fuels are renewable energy sources. The combustion of biomass and biomass-derived fuels is CO₂-neutral and can be seen as a primary measure to reduce this greenhouse gas. To obtain a sustainable and clean environment, the utilization of these fuels has to be increased and this is an important issue of global energy strategies. Besides these advantages, a possible drawback of these fuels combusting in an FBC might be that the nitrogen of the fuel is converted in relatively high amounts to NO and to a lesser extent to N₂O,^{1,2} because the lower operating temperature will lead to more nitrous oxides (N₂O) emission. Therefore, from this viewpoint, an FBC that combusts the biofuel is a versatile and relative clean technology except with respect to NO and N₂O emission.³ As we all know, NO is a harmful pollutant causing direct injuries of the respiratory organs and is the precursor for acid rain and ground-level ozone. N₂O is a very strong greenhouse gas and destroys ozone in the stratosphere. Meanwhile, NO is also an

intermediate in the formation of N₂O in combustion systems.³ Moreover, NO_x is known to play a role in the formation of photochemical smog, too. The low combustion temperature, however, enhances the formation of N₂O ranging from 15 to 200 ppm in comparison to levels observed in pulverized coal combustion boilers at 5 ppm.⁴ In the FBC, the oxidation of fuel-N of fossil fuels is the major source of NO formation.^{5,6} Therefore, fuel properties and operating conditions in an FBC are significant parameters for NO and N₂O emission. Generally speaking, NO emissions increase with bed temperature^{5,7–9} and excess air ratio.^{8,10,11} Most studies, including recent reports,^{3,4,12–17} are aiming at the conventional bubbling fluidized bed combustor,

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the pressurized fluidized bed combustion (PFBC), and the circulating fluidized bed combustor (CFBC).

In order to improve the performance of the FBC, a vortexing fluidized bed combustor (VFBC), an integration of bubbling fluidized bed and cyclone, was developed early in the 1970s.¹⁸ The first pilot scale VFBC was constructed and operated by Korenberg.¹⁹ It was modified and renamed by Nieh and Yang²⁰ later. The concept of the VFBC is to establish a vortex-generating system by injecting the second air tangentially into the freeboard to increase the combustion intensify, the calcium utilization, and the turndown capability. The advantages of low pollutant emissions and high combustion efficiencies by operating a VFBC have been demonstrated for combustion of waste tires in the previous study. We have reported the NO emission in a vortexing fluidized bed combustor in our recent paper.²¹ In this paper, the inner diameter of the combustor, including the combustion chamber and the freeboard, is 0.45 m, and it is found that the excess air is the most important factor to dominate NO emission and that NO emissions can be reduced by adding soybean to the fuels. However, this paper has not studied the characteristics of the N₂O emission.

The main purpose of this study is to understand the effect of operating conditions, such as bed temperature, excess air, fuel property, and the method of temperature control on NO and N₂O emissions operated in a pilot scale vortexing fluidized bed combustor. In order to improve the combustion efficiency further, the geometry of the combustion chamber is retrofitted in this study, i.e., the cross section of the combustion chamber is 0.64×0.32 m², and the inner diameter of the freeboard is 0.45 m. The concentrations of NO and N₂O at various distances from the distributor within the combustor chamber is recorded and analyzed. Knowledge is gained about the relationship between the composition of fuel and NO and N₂O emissions in order to develop efficient strategies for NO and N₂O reduction for a clean and sustainable environment.

2. Experimental Section

2.1. Experimental Apparatus. A process flowchart of the VFBC combustion system used in this study is shown in Figure 1. The fluidizing air as well as the primary combustion air is supplied by a 15 hp Root's blower. The second air is supplied by a 7.5 hp turbo blower. Four equally spaced second air injection nozzles with diameters of 12 mm are installed tangentially at a level of 1.3 m above the distributor to cause the swirling flow in the freeboard. A 20 hp compressor is used for transporting the feed through a pipe into the combustor.

Figure 2 shows the configuration of the VFBC used in this study. The VFBC is made up of four parts, i.e., the windbox, the distributor, the combustion chamber, and the freeboard. The combustion chamber with cross section 0.64×0.32 m² is constructed of a 6 mm stainless steel covered with the ceramic fiber to limit the heat loss. A windbox with cross section 0.64×0.32 m², connected to the air supplied line, is fabricated of 6 mm stainless steel. Above the combustion chamber, the inner diameter of the freeboard is 0.45 m. The static bed height is 0.3 m. Thirty-one horizontal nozzles with diameters of 6.8 mm mounted on a 6 mm thickness stainless steel plate are used as the gas distributor (the

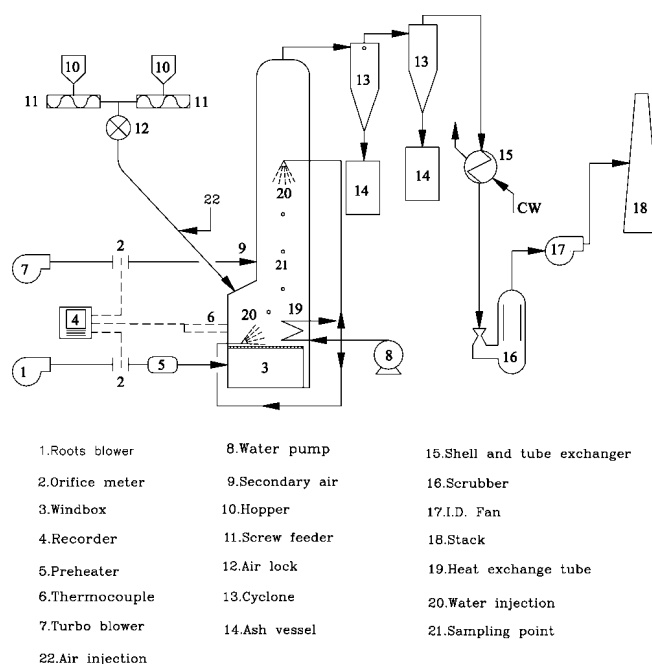


Figure 1. Flow diagram of the VFBC combustion system.

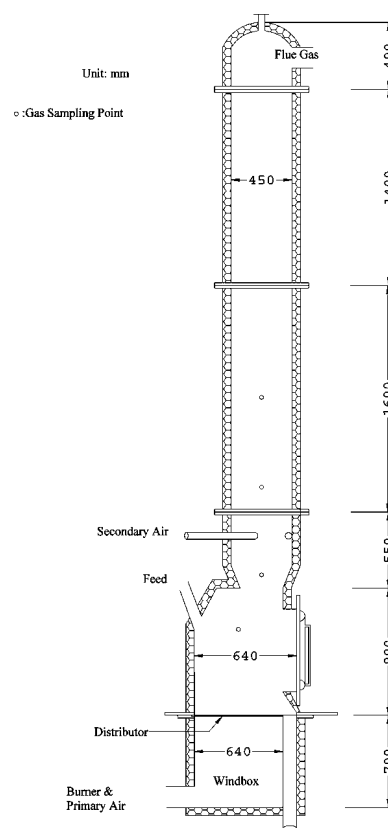


Figure 2. Configuration of the VFBC.

open area ratio is 0.55%). The horizontal nozzles are arranged on a triangular pitch and all the directions of the nozzles are the same.

The temperature and pressure drop in the VFBC are measured with a K-type thermocouple and the manometers connected to the pressure taps located along the wall of the combustor, respectively. The bed temperature is controlled by the water injection and heat-transfer tube immersed in bed. The flue gases are sampled at 0.6 (above the bed surface), 1.0 (below the inlet of second air), 1.65 (above the inlet of second air), 2.3 (within the freeboard), and 7.1 m (above the first cyclone) above the gas distributor. The components of the flue gas, such as N₂O, CO, CO₂, O₂, and NO are analyzed by an MTI-M200 micro gas chromatograph (GC) (N₂O, CO₂) and

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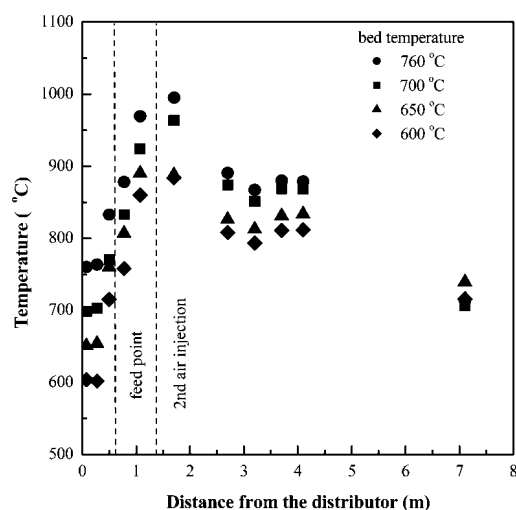


Figure 3. Axial temperature distribution in the VFBC at various bed temperatures (fuel = rice husk; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

Table 1. Properties of Fuels

fuel	rice husk proximate analysis (wt. %)	soybean	high sulfur coal
moisture	11.00	11.00	18.9
volatile	58.75	74.33	31.37
fixed carbon	14.30	6.06	45.36
ash	15.95	8.61	4.37
ultimate analysis (wt. %)			
carbon	33.19	41.6	48.85
hydrogen	4.38	6.49	5.68
oxygen	33.87	27.45	21.2
nitrogen	1.00	4.39	0.54
sulfur	0.61	0.44	0.46
ash	15.95	8.61	4.37
H ₂ O	11.00	11.00	18.9
N/C	0.228	0.106	0.011
O/N	33.87	6.25	39.26
H/N	4.38	1.48	10.52
wet base low heating value (kcal/kg)			
	3365	4595	5172

MSI 2000 chemiluminescent gas analyzers (O₂, CO, NO), respec-

Table 2. Experimental Conditions

Operating Parameters	
bed temperature range (°C)	600~760
superficial velocity (m/s)	0.66~1.15
primary air rate (Nm ³ /min)	1.98~3.4
second air rate (Nm ³ /min)	0~2.07
excess air (%)	20~90
Bed Material—Silica Sand	
bed material	silica sand
density of bed material (kg/m ³)	2500
mean diameter (μm)	486
bed weight (kg)	100

tively. Gas samples are drawn out from the combustor, cooled, and then passed through the above analyzers. The dry process is carried out within the analyzers. The values of the concentrations reported in this study are all corrected to 10% residual oxygen on a dry basis.

2.2. Fuels and Bed Materials. The overbed feeding system is employed. The fuels stored in two hoppers fall directly through

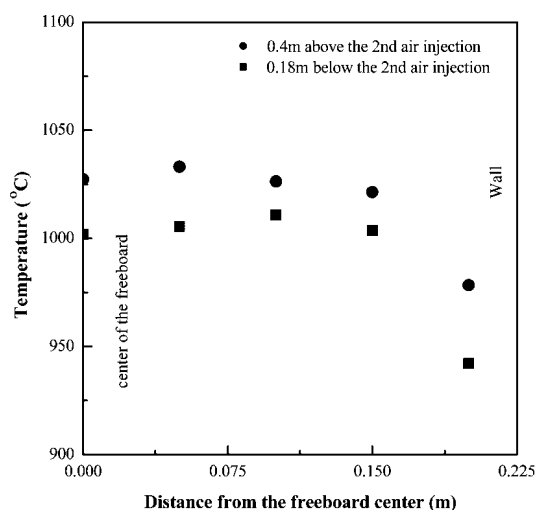


Figure 4. Radial temperature distribution of the various radial distances (fuel = rice husk; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

the screw feeders and an air lock and, then, by a 70° cooled chute into the fluidized bed chamber at 0.6 m above the distributor. Rice husk, soybean, and high sulfur sub-bituminous coal are used as the feeding material. The total heat (wet base) feed is kept as 150 00 kcal/h. The proximate and ultimate analyses of feeding material are listed in Table 1.

Flue gas leaving the combustor enters two cyclones arranged in series for the primary cleaning. Ash and unburned char drop from each cyclone into a sealed vessel for removal and analysis. After exiting from the cyclone, the flue gas enters a shell-and-tube heat exchanger and then passes to a venturi scrubber. Finally, the flue gas is discharged via the stack.

Silica sand is employed as the bed material in this study. The sand particle size range is 163–920 μm, and the mean size of the sand is 486 μm in diameter. The operating conditions for experiments are shown in Table 2. It should be noted that we change the total excess air by changing the primary or the second air flow rate in our experiment. The following definitions were used:^{13,14}

$$\text{stoichiometry} = (\text{total air flow rate})/(\text{stoichiometric air flow rate})$$

$$\text{excess air (\%)} = (\text{stoichiometry} - 1) \cdot 100$$

3. Results and Discussion

3.1. Effects of Bed Temperature. A typical temperature distribution within the VFBC at different bed temperature is presented in Figure 3. Figure 3 shows that the temperature within the VFBC increases with an increasing bed temperature. The temperature in the freeboard is higher than that within the bed, and the highest temperature is found at the position above the second air injection. Figure 4 shows the radial temperature distribution at the freeboard. It can be seen that the temperature below the second air injection is lower than that above the second air injection. In the case of the second air injection by vortexing, the contact opportunity between oxygen and volatile increases due to the turbulence and, consequently, the temperature increases. A clear tendency also can be seen, i.e., the temperature close to the wall is lower than that close to the center of the freeboard. This can be attributed to the heat loss from the combustor wall.

Figure 5 shows the effect of the bed temperature on NO and N₂O emission when rice husk is used as the feeding fuel. Usually, the NO emission increases with the bed temperature. However, from Figure 5, we can find that it exhibits a leveling-off trend. This can be attributed to the adequate residence time within the combustor to reach the equilibrium of the formation and reduction reactions of NO.

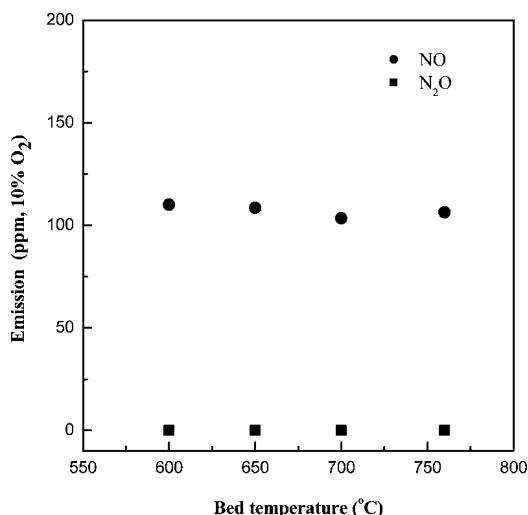


Figure 5. Effect of the bed temperature on NO and N₂O emissions at 7.1 m above the gas distributor (fuel = rice husk; primary air =120% stoichiometric air; second air =40% stoichiometric air).

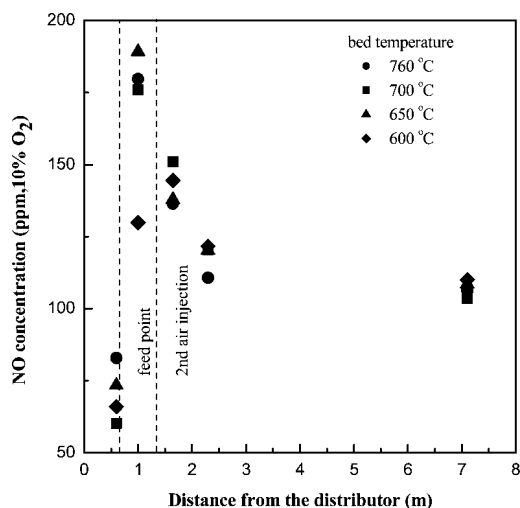


Figure 6. NO concentration profiles at various distances from the distributor (fuel = rice husk; primary air =120% stoichiometric air; second air =40% stoichiometric air).

In Figure 6, the concentrations of NO detected along the axial direction at various bed temperatures are very similar. The lowest concentration of NO appears above the bed surface. However, considerably high concentrations of O₂ and CO are detected above the bed surface as well.^{13,14} This implies incomplete combustion caused by poor mixing of fuel and gas. The low primary air flow rate, 120% stoichiometric air, results in local O₂ shortage.

The maximum concentrations of NO were detected at the region between bed surface and the inlet of second air except for operating at bed temperature of 600 °C. A lower concentration of NO detected within this region at 600 °C may be caused by that the low bed temperature retards the devolatilization rate of fuel.

The concentration of NO decreases abruptly, up to 50%, between the inlet of second air and 2.3 m above the distributor. This demonstrates a good atmosphere for NO reduction within this region. Carbon particles are captured by the swirling second air, and the reduction reaction of NO is preceded. In addition, a high concentration of CO participates in the reaction to reduce the NO concentration.⁹ Furthermore, the dilution by the second air also decreases the NO concentration.

From Figure 7, it can be found that the concentration of N₂O

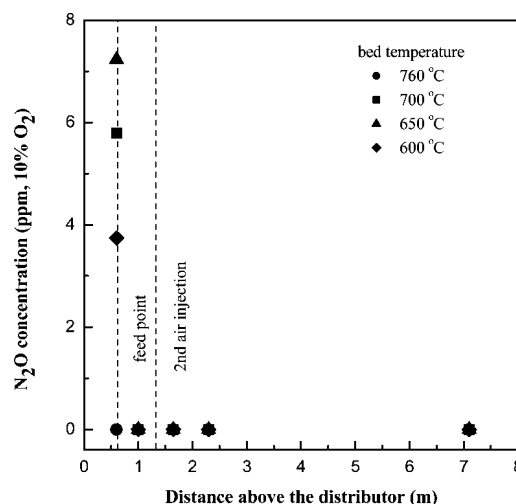
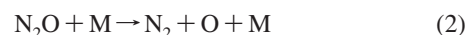


Figure 7. N₂O concentration profiles at various distances from the distributor (fuel = rice husk; primary air =120% stoichiometric air; second air = 40% stoichiometric air).

detected in the combustor is nearly zero no matter what the bed temperature is except for above the bed surface. Furthermore, no N₂O is detected in any position within the combustor at 760 °C. Generally speaking, N₂O can be detected only near the bed surface, where the fuel is fed. When the fuel particles entered the bed, a significant fraction of the volatiles was released near the fuel feed point (above the bed surface). Bearing in mind that an important precursor of N₂O are the volatiles,¹⁴ and the volatiles include HCN, NH₃, and HCNO. As the fuel particle heated up, its structure was ruptured and NH₃, HCN, and HCNO were released from the fuel and its tar. Then, NH₃ and HCN were oxidized in a complex reaction mechanism (mainly with O and OH radicals) to form NO.²² However, the formation of N₂O was delayed and started rather late, after the extinction of the flame. This behavior suggested that N₂O was destroyed in the flame mainly by the fast reaction (reaction 1) and to a lesser degree (nearly zero) by the thermal destruction mechanism (reaction 2) shown below:²



where M is any stable molecule (third body). In this paper, M mainly refers to the carbon particles and sands located between the bed surface and the secondary air inlet. These third bodies are circled by the swirling gas flow of the secondary air.

From the above analysis, and according to the experimental data obtained in this study, it can be stated that N₂O emission from the combustion of biomass can be neglected.

3.2. Effects of Excess Air. Figure 8 shows the effect of excess air on NO and N₂O emissions. From Figure 8, it can be found that NO emission increases with excess air. This is in agreement with the previous investigators' results.^{8,11,23} However, the effect of excess air on N₂O is not significant. It can be attributed to the fact that thermal decomposition reaction in the freeboard is the dominant factor for N₂O emission (See section 3.1).

The concentration of NO detected within the combustor is shown in Figure 9. It can be seen that all concentration profiles at various excess air show the similar trend as that shown in

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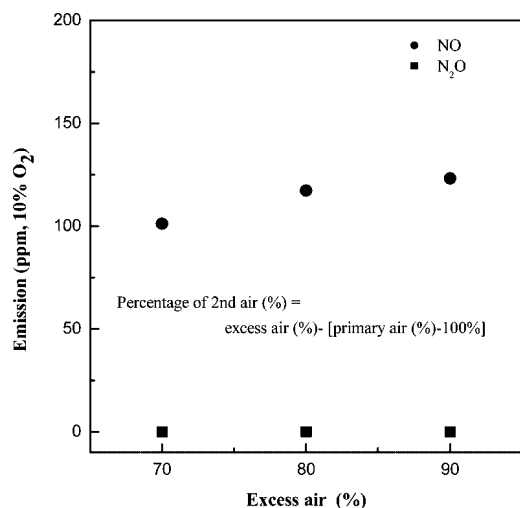


Figure 8. Effect of the excess air on NO and N₂O emission at 7.1 m above the gas distributor (fuel = rice husk; bed temperature = 650 °C; primary air = 120% stoichiometric air).

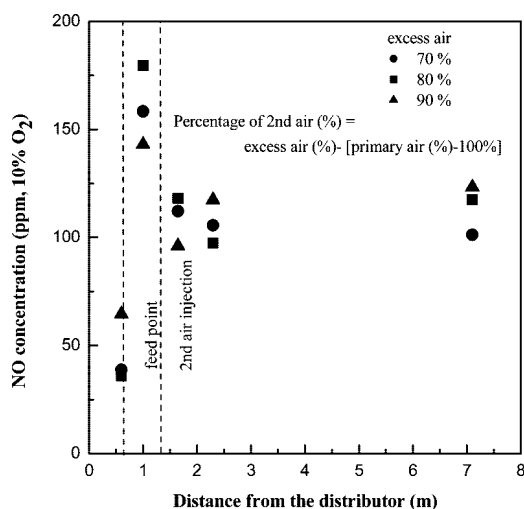


Figure 9. NO concentration profiles at various distances from the distributor (fuel = rice husk; bed temperature = 650 °C; primary air = 120% stoichiometric air).

Figure 6. Therefore, it can be deduced that most NO is formed within the region between the bed surface and the inlet of second air, then, is reduced considerably within the freeboard zone, and eventually reaches a lower concentration at outlet. It also can be seen that the NO concentration increases at 90% excess air when the flue gas enters into the freeboard. The possible reason is that the high oxygen concentration will result in the NO increase.²⁴ It should be noted that the concentration profiles in this study are different from those in the work of Chyang et al.²¹ The logic explanation could be that different fuels, fuel feeding positions, and low bed temperature will produce this difference.

The distribution profile of the NO concentration within the combustor along the axial direction at second air of 40% stoichiometric air is shown in Figure 10. Compared with Figure 9, it can be found that the concentration of NO detected within the region between the bed surface and the inlet of second air at fixed second air flow is lower than that detected at fixed primary air flow for a certain amount of excess air. Three reasons can be proposed: (1) The increase of the primary air increases the amount of silica sand and unburned carbon that entrain into

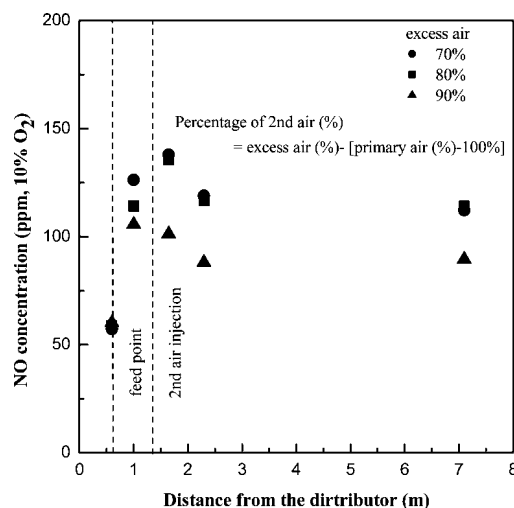


Figure 10. NO concentration profiles at various distances from the distributor (fuel = rice husk; bed temperature = 650 °C; second air = 40% stoichiometric air).

the freeboard, which are both good catalysts for NO reduction. At temperatures below 1000 °C, NO can be reduced by CO via heterogeneous reaction to N₂ and CO₂.^{13,14,21,25} Therefore, the reduction rate is enhanced while the amount of silica sand and unburned carbon within the freeboard increased caused by the increase of primary air. (2) The residence time of the components derived from the devolatilization of fuel decreases as the primary air flow increases. This causes the reaction zone (formation and reduction reaction) to move upward, and the maximum value of NO is detected at the second air injection zone.

3.3. Effect of Methods of Temperature Control. Two methods of temperature control, a heat-transfer tube and water injection in the bed and freeboard (2.15 m above the distributor), respectively, are employed in this study. The experiments are divided into three categories: (A) heat-transfer tube immersed in the bed; (B) heat-transfer tube immersed in the bed and water injected into the freeboard (0.14 L/min); (C) water injected into both the bed and freeboard (0.16 and 0.52 L/min, respectively). The concentration of NO detected at the bed temperature of 650 °C, primary air of 120% stoichiometric air, and second air of 40% stoichiometric air, with various methods for temperature control, are shown in Figure 11.

At the location of 1 m above the distributor (just below the inlet of second air), the concentration of NO detected in experiment C is obviously higher than that detected in experiments A and B. It is reasonable to say that a large amount of HCN and NH₃²⁶ forms from second pyrolysis of volatiles in this region and reacts with O, H, and OH radicals liberated from H₂O, which results in accelerated NO generation.² For experiment C, the concentration of NO around the location of the water injection nozzle keeps descending due to the temperature drop resulting from the water injected (see Figure 12), which decreases the generation rate of NO.

Only in experiment C (water injected into both the bed and the freeboard) is N₂O found above the bed surface (not shown in the figure). This is in contrast with the result of De Soete et al.²⁷ They suggested that OH radicals derived from H₂O possess

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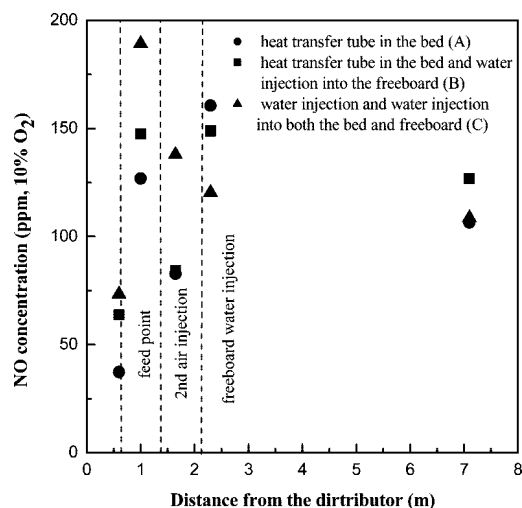


Figure 11. Effect of the different temperature control methods on the NO concentration profile detected at various distances from the distributor (fuel = rice husk; bed temperature = 650 °C; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

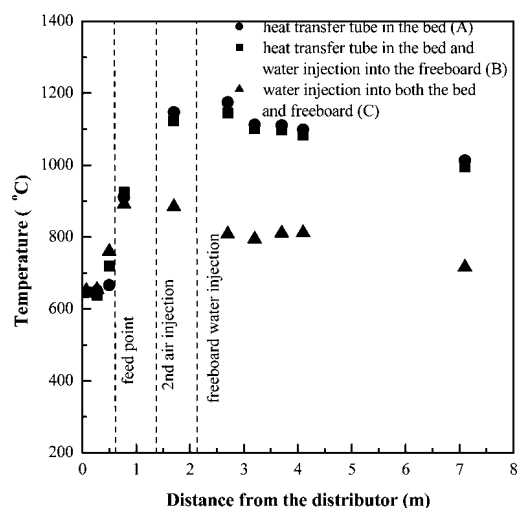


Figure 12. Axial temperature profiles with different bed temperature control methods (fuel = rice husk; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

the ability to decompose N₂O. However, Aho et al.²⁸ found a similar result, i.e., an OH radical cannot increase the decomposition of N₂O. Therefore, the relationship between N₂O decomposition and OH radicals derived from H₂O when water is injected in the bed is not distinct. In fact, liquid water vaporizes and expands rapidly as soon as water enters into the bed resulting in vigorous turbulence within the bed and increasing gas–solid contact. Hence, the reaction of NO with char-N on the surface of char to N₂O is promoted.²⁷ In addition, from the viewpoint of homogeneous reaction, the formation N₂O reaction rate of the intermediate species, NCO and NO, is associated with the vigorous turbulence.²²

3.4. Effect of Fuel Properties. The distribution of NO concentration within the combustor with various feeding material is illustrated in Figure 13. It is evident that most of the NO and N₂O was formed during devolatilization within the region between the bed surface and the secondary air inlet. Some early published papers^{29–31} considered that NO_x emission mainly came from oxidation of the char-N and volatile-N in fuels and

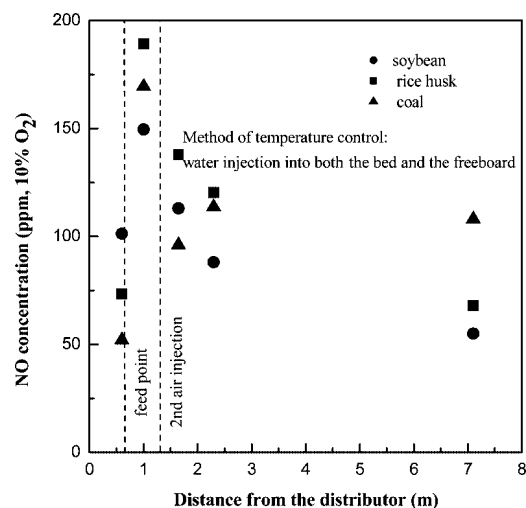


Figure 13. NO concentration profiles at various distances from the distributor with different fuels (bed temperature = 650 °C; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

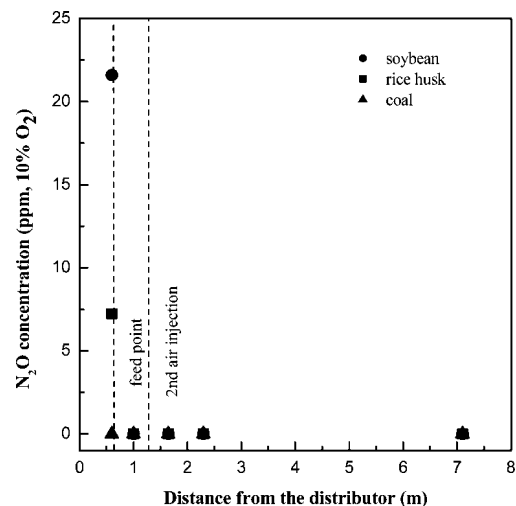


Figure 14. N₂O concentration profiles at various distances from the distributor with different fuels (bed temperature = 650 °C; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

that the volatile-N is the main source. Therefore, the formation of these species during char combustion is generally of low importance. This result is in agreement with other reports.¹⁵

From Figure 13, it can be seen that the concentration of NO is proportional to the volatile content of feed material (soybean is highest; coal is lowest) at the initial stage when fuels enter the bed. It was found that the conversion of fuel-N to NO increases with volatile-N in oxygen-rich conditions for coal combustion.³² Whatever the fuel, the maximal NO concentration takes place between the feeding point and the second air injection. However, from the second air injection on, the NO concentration distribution does not have a clear trend. One possible reason for this may be the effect of the water injection at the freeboard on the formation and reduction reaction of NO. Another logical explanation could be that the rice husk has a

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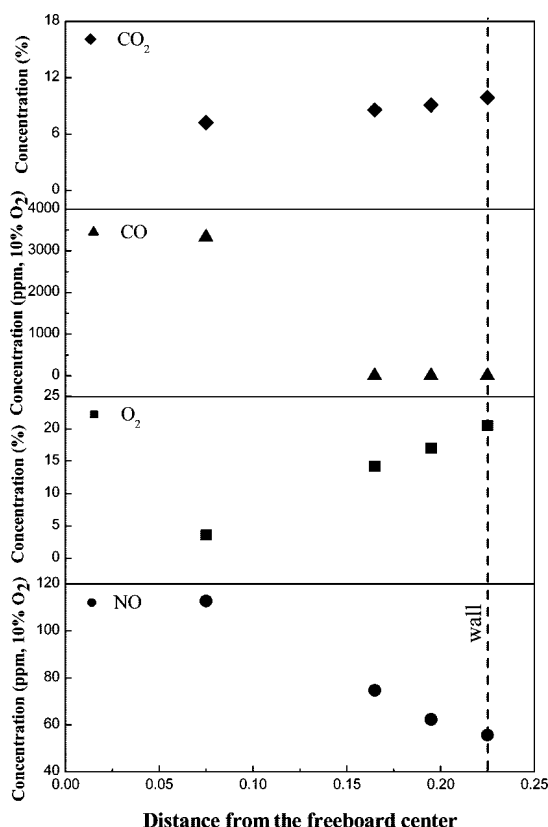


Figure 15. Concentration profile of various gas components along the radial direction within the freeboard at 2.3 m above the distributor (bed temperature = 650 °C; primary air = 120% stoichiometric air; second air = 40% stoichiometric air).

lower density, which makes it float into the freeboard and then conduct the devolatilization and combustion reaction there. At the outlet of combustor, NO emission from the combustion of coal is the highest. That is because HCN would convert to NH₃ and further to NO, via the process of fuel-NO generation. The amount of HCN generated from ring-type nitrogen-containing species (pyridine and pyrrole) in coal is much more than that in the other two kinds of biofuels. It was also stated that biofuel possesses a higher volatile content and, generally, volatile liberates rather NH₃³³ which would inhibit the formation of NO_x and N₂O, than HCN and other CN groups.

The N₂O concentrations of all fuels are zero except for the region 0.6 m above the gas distributor during devolatilization, and the distributions in the combustor are shown in Figure 14. In this study, for coal combustion, N₂O is not detected above the bed surface, which is the same as the finding of Tarelho et al.¹⁴ and contrary to other studies.^{3,17,34} Tarelho et al.¹⁴ stated that a logical explanation for the differences could be the different feeding position. It should be noted that the N₂O concentration at the freeboard reported here is inconsistent with the above results.^{3,14,17,34,35} The possible reason may be the long residence time (long freeboard in this study) for conducting the complex reduction reaction (see section 3.1). Moreover, the region near the second air injection has the highest temperature in the combustor (see Figure 3), and most destruction reactions

occur here. Additionally, different fuel properties also may produce this difference.

N₂O from the combustion of soybean above the bed surface is higher than that from rice husk. This is similar to the situation of NO. The higher the volatile content, the easier N₂O is formed at the initial stage. This demonstrates that the key point of the formation of nitrogen oxides is volatile-N, not char-N. This is in agreement with the result obtained by elsewhere.^{33,36} It was also suggested that the char from biomass is extremely active to N₂O owing to its porous nature,³⁷ so N₂O reduces readily.

3.5. Distribution of NO in the Radial Direction. Figure 15 shows the distributions of CO₂, CO, O₂, and NO in the cross section of the freeboard above the position of the second air injection nozzle (the position of the sampling point is 2.3 m above the distributor), while soybean is used as fuel.

From Figure 15, we can find that a high concentration of O₂ is detected near the wall of the combustor. However, the concentration of NO exhibits a contrary trend and CO only can be detected around the center of the freeboard. Moreover, N₂O is not been detected in this region.

The second air is introduced tangentially into the freeboard. Owing to the centrifugal force, air moves toward to the wall, resulting in a higher concentration of O₂ near the wall. Similarly, when NO and CO are formed in the center region of the combustor, the second air which produces the swirling flow in the freeboard will cause these gaseous to move toward the wall, consequently resulting in the distribution profiles in Figure 15. CO₂ distribution profile can be explained by the oxidation and deoxidization reaction of the CO. The reason may be the following reaction mechanism:^{38,39}



Where, C(O) refers to a surface carbon–oxygen complex and C* represents a “free” active life for NO reduction. Additionally, it is noted that the radial CO₂ and O₂ concentrations seem to be complementary to each other. However, the sampling position is located 1 m above the second air injection so that much O₂ may not react with the volatiles and enter into this position, which results in the higher O₂ concentration at this position.

4. Conclusions

The investigation of NO and N₂O emission has been conducted in a pilot scale vortexing fluidized bed combustor for three fuels. Experiments were conducted to investigate the effects of various operating conditions, such as bed temperature, excess air, fuel property, and the method of temperature control on NO and N₂O emissions. The results show that NO emission increases with excess air and is almost independent of the temperature of the bed (600–760 °C). NO and N₂O emissions are influenced by the method of bed temperature control. Water injected into the bed would lead to the increase of NO and N₂O within the combustor chamber. A concentration gradient of NO in the radial direction can be found within the freeboard. The

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concentration of NO decreases as the distance from the wall decreases. The fuel material with high volatile content appears to form a significant amount of NO and N₂O above the bed surface, while NO emission decreases with volatile content at the outlet of the combustor. Most NO is formed above the bed surface, achieves a maximum value at the position below the

second air injection, and is reduced considerably within the freeboard. Moreover, the most remarkable feature is that N₂O emission from the combustion can be neglected no matter what the feeding material is.

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