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Reduction of Nitrogen Oxides from Fuel Nitrogen in New Fuelling System

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The effects of NO_x reduction by advanced fuel staging in a small scale combustor (6.6 kW_T) have been investigated using propane gas flames laden with ammonia as fuel-nitrogen. The variables which had the greatest influence on NO_x reduction were temperature, reducing stoichiometry (relative to main combustion zone stoichiometry, air fraction and reburning fuel fraction) and residence time of reducing zone. NO_x reduction was best at the reburning zone temperature of above 1,000 °C and reburning zone stoichiometry was 0.85. In terms of residence time of the reburning zone, NO_x reduction was effective when burnout air was injected at the point where the reburning zone had been already established. In the advanced fuel staging NO_x reduction was relatively large at the burning of higher Fuel-N concentration in the fuel. Under optimum reburning conditions, fuel nitrogen content had a relatively minor impact on reburning efficiency.

Introduction

Nitrogen oxides (NO_x) has been recognized as air pollutants for decades due to its effects on human and animal health, damage to vegetation and the role of NO_x in producing smog.

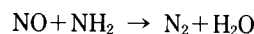
Staged combustion has been demonstrated as an effective method for reducing nitrogen oxides emission.¹ Under staged combustion condition locally fuel rich zones develop in the

flame in which fuel bound nitrogen species react with NO to produce molecular nitrogen. The conversion degree of which the FBN (fuel bound nitrogen) conversion to N₂ is successful is determined by the thermodynamics of the system, and the rate of reactions in the fuel rich flame zone.^{2,3}

The nitrogenous compounds in the reducing zone may have two different origins:

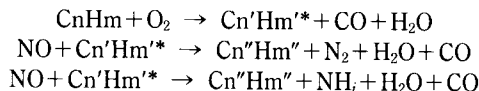
In the first one of air two staging, they react in rich flames to form intermediates such as NH₃ and HCN in post-

flame gases and that some of these are then oxidized (probably by OH radicals) to form NO. The NO_x further reacts by a reaction such as



If the rate of destruction of NO can be kept high relative to its rate of formation, low fuel-NO will be achieved.⁴ Operation closed to the rich limit presumably reduces the OH concentration in the primary flame and the rate of formation of NO is thereby reduced there.

In the second one of staged fuel injection, the NO containing lean burned gas reacts with hydrocarbon fragments such as CH₂ to produce HCN and NH_i (*i*=3, 2, 1) compounds in a flame zone which is turned fuel rich by addition of the reburning fuel. This process in the reburning zone was also shown by Takahashi *et al.*⁵ as follows:



Where the asterisks (*) denote a radical at the initial stage of chemical reaction and NH_i represents any nitrogen compounds.

Wendt *et al.*,⁶ who in that pioneering work studied NO reduction by secondary fuel injection in a laboratory flat flame introduced the term "Reburning" for this method of NO reduction. Myerson⁷ using a ceramic laboratory scale reactor demonstrated extensive reduction of NO in combustion effluents by the addition of hydrocarbon mixtures in the temperature range of 1200 to 1700 K. They confirmed that the principal product of reaction was N₂ with HCN as the secondary product. Clark *et al.*⁸ using pulverized coal as secondary fuel in laboratory scale experiment found that even a nitrogen bearing fuel like coal can be used as a reburn fuel effectively as long as the primary NO concentration was high. Practical application utility boilers have been reported by Mitsubishi Heavy Industries. Their system of over fire fuel and air was offered under the trade name of MACT and was reported to be capable of reducing NO emission by 50%.⁹

As the above-mentioned, there are many studies about the conventional fuel staged combustion which is three stage Lean-Rich-Lean. However in the case of these method the NO_x formation of the primary lean zone is increased by oxidizing atmosphere particularly with higher fuel bound nitrogen fuel. And NO_x of burnout zone is increased by quenching effect¹⁰ because of burnout air.

Consequently, there is a need for a new approach that the primary lean zone is divided into Rich-Lean (to reduce NO in the main combustion gas) with another set of rich-lean stages which is four stage Rich-Lean-Rich-Lean as seen in Figure 1. It is the intent of the studies described in this paper to examine the parameters controlling the effectiveness of advanced fuel staging by conducting a series of bench scale reactor studies with well defined conditions in the NO reduction and the TFN (total fixed nitrogen; NH₃, HCN and NO) oxidation zones.

Experimental

The experimental apparatus, shown in Figure 2, is a small-

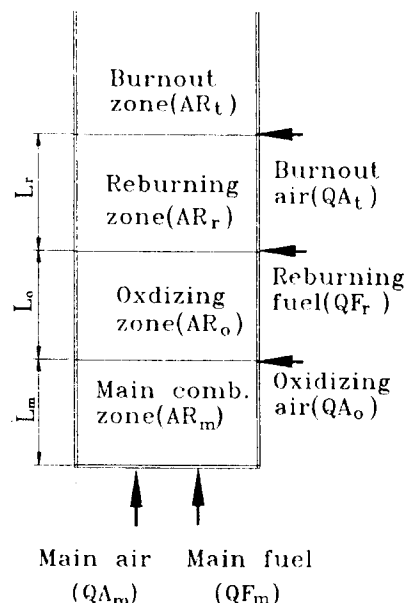


Figure 1. Schematic of different staging configuration.

scale (6.6 kW_T) test rig.

The furnace was designed to satisfy two general criteria; to allow adequate control of the gaseous environment, and to provide ready access for several physical diagnostic system.

Main burner is formed the coaxial diffusion flame and adapted the rim type for the purpose of stabilizing the flame. It is fired within the insulated stainless-steel reactor to minimize heat loss and external influences. It has four injection points for reburning fuel and secondary air. At each point four symmetrically spaced radial jets of reburning fuel and secondary (oxidizing and burnout) air could be injected into hot products of the main combustion for fast mixing. For measuring temperature and gas concentration, it was designed 11 sampling ports in the surface of the reactor vertically.

Pure propane is used as main and reburning fuel. In some experience, pure ammonia was added to the fuel as fuel bound nitrogen to know the effects of fuel NO. The reason of which it was used ammonia as fuel-N are as follows, Firstly, during devolatilization of coal a part of fuel nitrogen is released with the pyrolysis gases. The volatile nitrogen quickly forms the intermediate species NH₃.

Depending on the fuel/air ratio and on temperature, the NH₃ is either reduced to molecular nitrogen or it forms NO. Therefore for the gas phase reaction of coal combustion it is useful to use NH₃ as fuel-N. Secondly, gasification fuel from coal contains NH₃ in great quantity.

The effects and mechanism of NO_x reduction and production were to be investigated about various parameters which were temperature, stoichiometry, residence time and reburning fuel composition as shown in Table 1. Tests were conducted such that the AR_m was changed from 0.5 to 1.4 while the AR_r was kept constant throughout each experiments. The combustion products and the temperature were measured at 11 points upper the burner. A complete set of measurements was not made on any one run. Runs typically lasted more 1 hour and covered a range of stoichiometric ratio.

The gas species sample was collected using a water-cooled

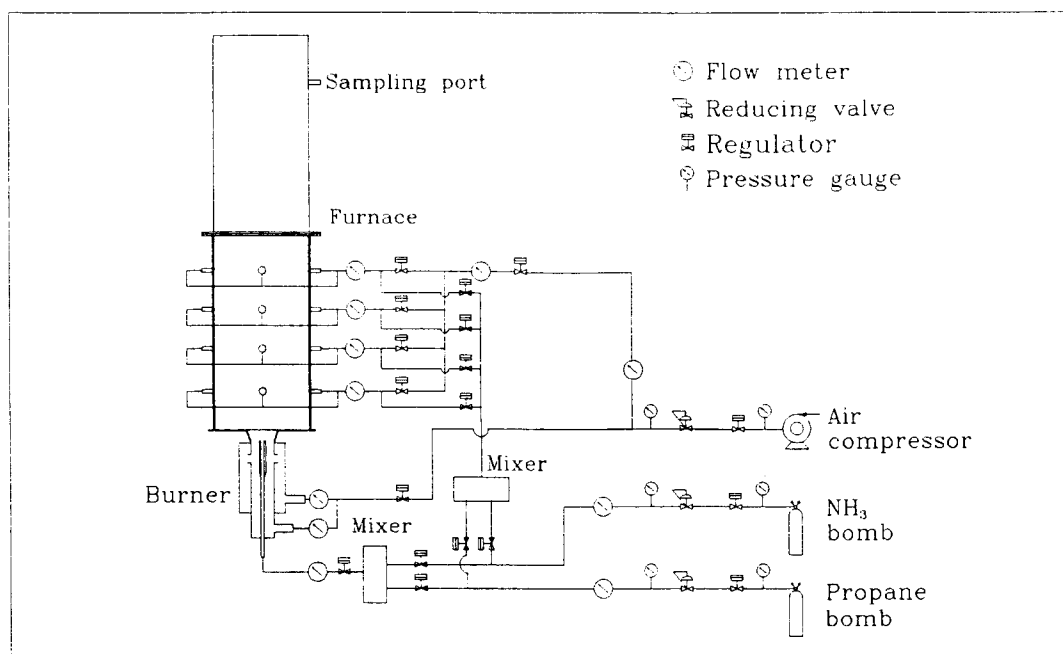


Figure 2. Schematic of flow system.

Table 1. Experimental and reference parameters

	Parameters	Reference parameters
Total air ratio (AR_t)	1.1, 1.2, 1.3, 1.4	1.1
Reburn fuel fraction (F)	14, 25, 50%	25%
Air fraction (A)	25, 50, 75%	50%
Residence levels of the all zone (L_m , L_n , L_r)	1.0, 2.0	1.0
Fuel-N addition to the main fuel (FN_m)	0, 1.0, 1.5, 2.0%	0, 1.0%
Fuel-N addition to the reburn fuel (FN_r)	0, 1.0, 1.5%	0%
Temperature of the reburning zone (T_m)	insulated, Non-insulated	Insulated

stainless probe. They were filtered and dried before measuring O_2 , CO and CO_2 by gas chromatography, and the measurement of NOx was carried out using a chemiluminescent analyzer. HCN and NH_3 were measured by an ion-electrode method.¹¹ Since NH_3 and HCN were easily absorbed by water, all of the sampling line was heated up to between 100 °C and 150 °C by a ribbon heater, and warmed silicone oil was used as a coolant for the sampling probe instead of water. The time mean temperature was measured with a fine, bare (Pt/Pt13%Rh, 0.1 mm) thermocouple. The results were corrected for radiation error.

Results

Experiments were conducted in the propane flame laden with Fuel-N as a main source of fuel-NOx to examine the effect of NOx reduction on advanced fuel staged combustion. The results presented here address two main topics; mecha-

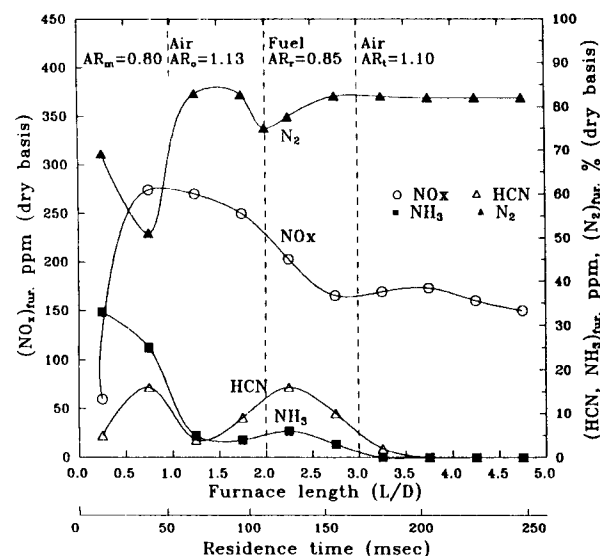


Figure 3. Furnace NO_x, HCN, NH₃ and N₂ for $AR_r=0.85$ ($F=25\%$, $A=50\%$, $L_m=1.0$, $L_n=1.0$, $L_r=1.0$, $FN_m=1.0$ wt%, $FN_r=0.0$ wt%).

nism of NOx production and reduction and parameter screening studies of NOx reduction.

Mechanism of NOx production and reduction

NOx, NH_3 , HCN and N₂ levels is shown in Figures 3 with $AR_r=0.85$. A large NOx peak is observed by the injection of secondary air, which thereafter decays throughout the reburning zone. HCN increases in the fuel-rich zone, but at a lower level. NH_3 decreases drastically at near the burner and does not exhibit any strong peak. N₂ concentration increases with the decrease of NOx in the reburning zone. The reason which increased NOx gradually in the main combustion, is that at the fuel-rich atmosphere of main combustion

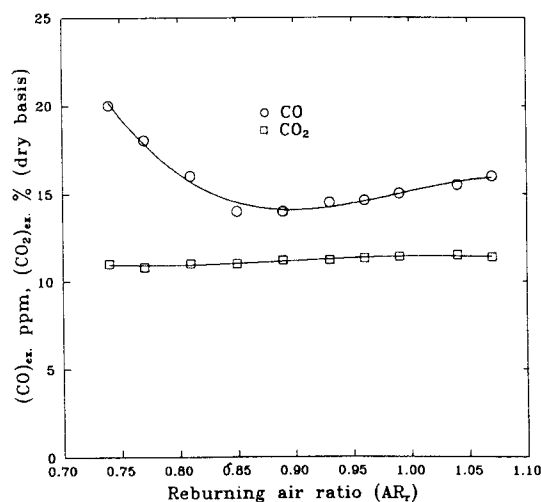


Figure 4. CO and CO₂ concentration at exit ($F=25\%$, $A=50\%$, $L_m=1.0$, $L_v=1.0$, $L_r=1.0$, $FN_m=1.0$ wt%, $FN_v=0.0$ wt%).

zone Fuel-N is converted to N-intermediates or N₂. Fenimore¹² also observed the passage of a relative N-intermediate through flames near the fuel-rich limit. After this region the NO_x emission is constant mostly. However the reburning fuel is injected downstream of the oxidizing zone to create a fuel-rich, NO_x reducing zone. NO formed in the main heat release zone reacts with hydrocarbon free radicals during the oxidation of the reburning fuel to produce intermediate species such as HCN and NH₃, and non-pollutant species, N₂. In the reburning zone, most of the NO produced in the main heat release zone is effectively reduced to N₂. In the burnout zone, additional combustion air is added to oxidize any remaining fuel fragments and produce overall fuel-lean conditions. The remaining reduced nitrogens species (NH₃ and HCN) are either oxidized to NO or reduced to N₂. Successful application of the staging concept requires that the reduction in concentration of the NO achieved in the reburning zone be preserved in the burnout zone. This in turn requires that the temperature in the burnout zone be controlled below values at which Zelovich NO formation rates are appreciable (1,800 K).

Figure 4 shows the variation of CO, CO₂ concentrations at exit according to the stoichiometric ratio of reburning zone (AR_r) with $AR_v=1.1$. CO emissions are an index of combustion efficiency. CO emissions increased slightly at low stoichiometric ratio due to incomplete mixing. However, as the stoichiometric ratio of the reburning zone was increased to the optimum level for NO_x emission control, CO emissions decreased at a minimum. CO₂ concentration was about 11%. Throughout the experiments, the profiles of exhaust gas concentrations were similar to those described above.

Parameter screening studies of NO_x reduction

Reactant Stoichiometry. Figure 5 shows the variation of NO_x concentration according to reactant stoichiometry.

For propane-air flames with no fuel-N added, little thermal-NO_x decreased as AR_v increased from 1.1 to 1.4 because maximum temperature was decreased. Thermal-NO_x emission in this furnace was very low because of its low flame-temperature. Through this study, combustion was achieved

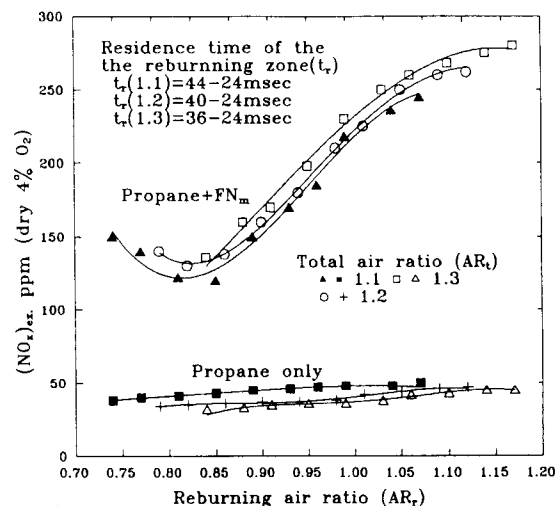


Figure 5. Effect of reactant stoichiometry on NO_x at exit ($F=25\%$, $A=50\%$, $L_m=1.0$, $L_v=1.0$, $L_r=1.0$, $FN_m=1.0$ wt%, $FN_v=0.0$ wt%).

lower than the temperature (1800 K) explained in terms of thermal-NO formation, *i.e.* Zelovich kinetics.

For propane-air flames with fuel-N added, the NO_x profiles according to AR_r are almost similar. Because the increasing of AR_r means the increasing of stoichiometric ratio in oxidizing and burnout zone, little fuel-NO_x was increased by oxidizing it with Fuel-N and so it was almost independent of AR_r . The required stoichiometry for optimization of the NO_x reducing zone is an important parameter because it establishes the amount of fuel which must be added to this zone and it controls the composition of the reactants entering the burnout zone. As AR_r decreased gradually, the exhaust NO_x was reduced drastically until at the optimum stoichiometry ($AR_r \approx 0.85$) regardless of AR_v . The percentage NO_x reduction was achieved 70 percent relative to baseline levels at AR_v of 1.1. Further decreases in AR_r cause an increase in the exhaust NO_x. The purpose of the NO_x reducing zone is to react the nitric oxide leaving the oxidizing zone with hydrocarbon radicals (such as CH, CH₂, CH₃) provided by the reburning fuel. In addition, there appears to be considerable interconversion of nitrogen among different N-intermediates. At AR_r less than 0.85, NH₃ and HCN formation becomes significant. Further these data demonstrate that as reburning zone stoichiometry was reduced, the NO_x increased dramatically. From these result it could be concluded that the best NO_x reduction is at AR_r of 0.85 and reburning zone stoichiometry is an important parameter regardless of AR_v .

Reburning fuel fraction. Most of the advanced fuel staging data was taken at a reburning fuel fraction of 25 percent, where 25 percent of total fuel was injected into the injection port of reburning fuel. This reburning fuel fraction (F) value was chosen as the nominal condition because the effect of fuel staging was expected to be significant and easy to see at this condition. Figure 6 compares the results of NO_x when F 's are 14, 25 and 50 percents. Throughout reburning stoichiometric ratio, NO_x emissions were less for $F=50\%$ than for $F=14\%$ and particularly at $AR_r=0.85$. It is the reason that the increase of reburning fuel means the increase of hydrocarbon free radicals which react with NO

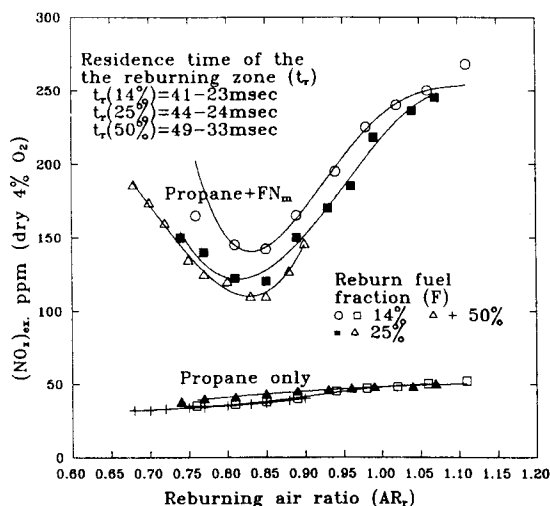


Figure 6. Effect of reburn fuel fraction on NO_x at exit ($\text{AR}_i = 1.1$, $A = 50\%$, $L_m = 1.0$, $L_o = 1.0$, $L_r = 1.0$, $\text{FN}_m = 1.0$ wt%, $\text{FN}_r = 0.0$ wt%).

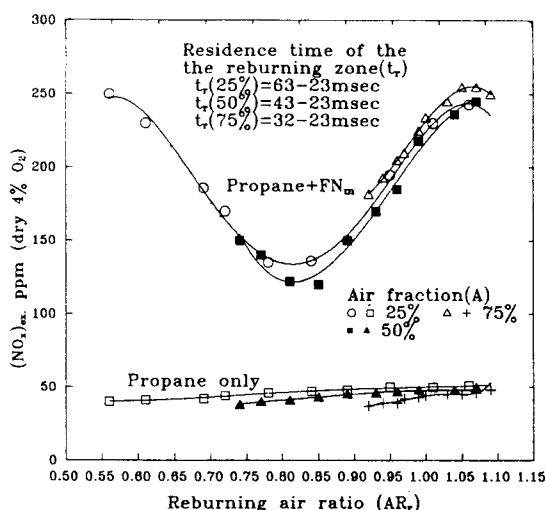


Figure 7. Effect of air fraction on NO_x at exit ($\text{AR}_i = 1.1$, $F = 25\%$, $L_m = 1.0$, $L_o = 1.0$, $L_r = 1.0$, $\text{FN}_m = 1.0$ wt%, $\text{FN}_r = 0.0$ wt%).

to be reduced to N_2 . However the NO reduction potential of fuel staging is not sensitive to fuel fraction by increasing the F values because of not good burning. This result was also shown by Bartok.¹³ The observed impact of fuel fraction, on NO performance can be interpreted by considering the limits of what would happen in all of the fuel is burned in the main combustion zone or reburning zone. Since residence time is limited in commercial system, most of the fuel is burned in the main combustion zone, particularly in the case of fuels which contain considerable bound nitrogen, such as coal and some oils. It is concluded that in commercial system F is decided the optimum point although NO reduction is achieved with the increase of F .

Burnout air fraction. Figure 7 show the variation of NO_x concentration according to the burnout air fraction. In this study, most of the data were taken at $A = 50\%$, where 50 percent of amounts except main combustion air among total air, was injected into oxidizing air injection port. The maximal NO_x reduction at the exit was achieved at A of

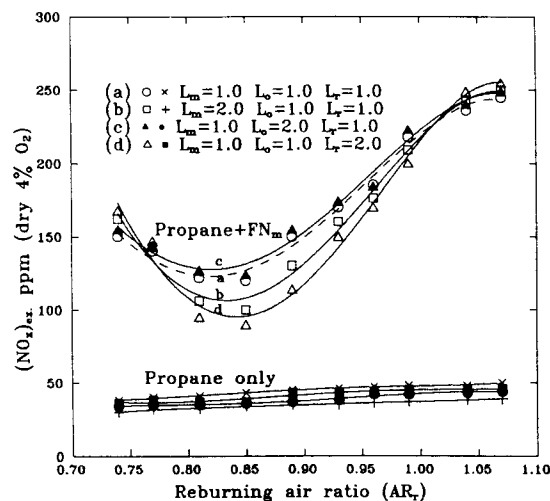


Figure 8. Effect of residence time on NO_x at exit ($\text{AR}_i = 1.1$, $F = 25\%$, $A = 50\%$, $\text{FN}_m = 1.0$ wt%, $\text{FN}_r = 0.0$ wt%).

50 percent with $\text{AR}_r = 0.85$. These data suggest that A is the best value which can be achieved at AR_r of 0.85 by injecting the oxidizing air. It is also reasonable that in this condition the NO from the main combustion zone can be converted to N_2 well because the temperature of oxidizing zone is not decreased by quenching as divided the secondary (oxidizing and burnout) air. In the advanced air staging, the conversion of fuel bound nitrogen was controlled through progressive air addition along the flame axis.¹⁰

Residence time. Figure 8 shows the variation of exhaust NO_x according to residence time. Most of the advanced fuel staging data were taken at nominal condition ($L_m = 1.0$, $L_o = 1.0$, $L_r = 1.0$) as shown in Figure 8a. Figure 8b shows the exit NO_x variation for different residence time of main combustion zone at fixed others. NO_x reduction was achieved with increasing the t_m under reducing atmosphere, and particularly at AR_r of 0.8 it was best NO_x reduction through NO_x formation like Figure 3. These results indicate that the reaction, that TFN is converted to N_2 , has been achieved enough with the increase of residence time in this region. Figure 8c shows the exit NO_x variation for different residence time of oxidizing zone at fixed others. NO_x levels were insensitive with increasing the t_o , although this zone was formed at oxidizing atmosphere. It is the reason that NO formed already this zone was converted almost to N_2 through the reburning region. Figure 8d shows the exit NO_x variation for different residence time of reburning zone at fixed others.

By increasing the residence time of reburning zone which was fuel-rich condition, the effect of NO_x reduction was very sensitive, and particularly at AR_r of 0.85. These data mean that TFN formed already have a greater opportunity to convert to molecular nitrogen, N_2 , rather than NO at the reducing zone and particularly at AR_r of 0.85. As can be known in previous study,^{5,14} for reducing the NO it reacts with radicals which was already formed from hydrocarbon fuel at reducing atmosphere. Therefore the increase of radicals in the reburning zone means more NO_x reduction. As discussed before, the increase of reburning zone give a chance to form the radicals by which hydrocarbon reacts with oxygen in

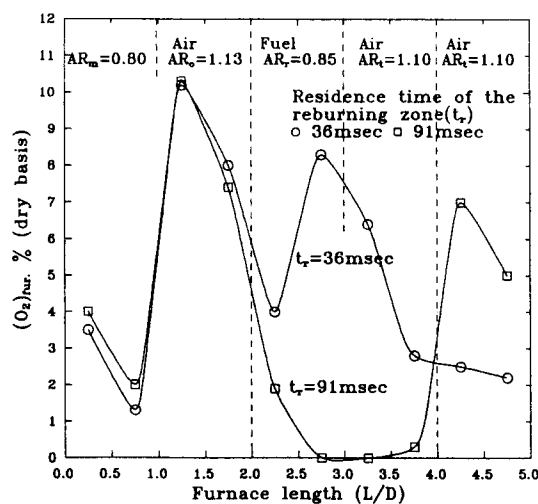


Figure 9. Furnace O_2 for $AR_r=0.85$ according to the residence time of reburning zone ($F=25\%$, $A=50\%$, $L_m=1.0$, $L_o=1.0$, $FN_m=1.0$ wt%, $FN_r=0.0$ wt%).

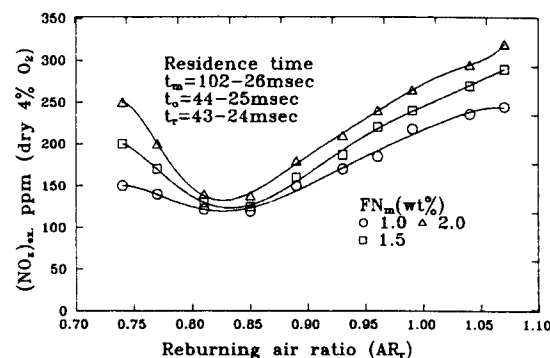


Figure 10. Effect of main Fuel-N concentration on NO_x at exit ($AR_r=1.1$, $F=25\%$, $A=50\%$, $L_m=1.0$, $L_o=1.0$, $L_r=1.0$, $FN_r=0.0$ wt%).

the combustion air. As can be seen in Figure 9, by increasing the t_r , oxygen concentration was almost consumed because of reacting with radicals. In these studies, the effectiveness of the reduction increased when the oxygen in the combustion gases was depleted by reburning fuel injection. Maximum reduction was observed when the amount of fuel exceeded the available oxygen limit. Also these results were known by this authors¹⁵ from the small scale test (5.5 kw) of air two staging with pulverized coal. From above results it should be noted that for the $AR_r=0.85$ case the level and reduction of NO_x is intensive with the increase of t_r .

Fuel-N concentration. The effect of NO_x emissions according to the Fuel-N concentration is shown in Figure 10. The best NO_x reduction was achieved at AR_r of 0.85 and NO_x concentrations according to Fuel-N concentration was very similar regardless of Fuel-N concentration although in the earlier studies¹⁶ NO_x level increased with the increase of Fuel-N concentration in conventional fuel staging. It is of special interest that in the case of advanced fuel staged combustion the impact of the NO_x reduction is relatively large at the burning of higher Fuel-N concentration in the fuel.

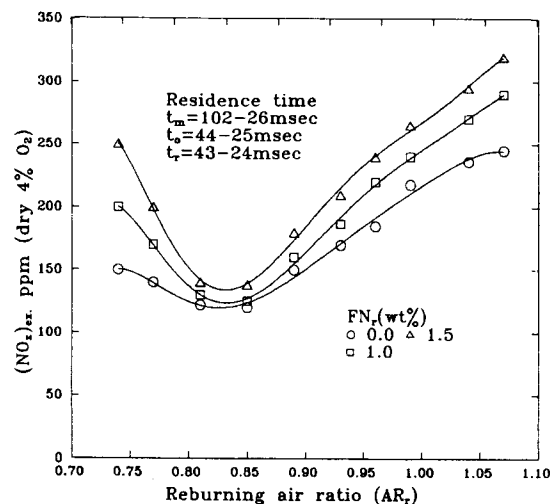


Figure 11. Effect of reburning Fuel-N concentration on NO_x at exit ($AR_r=1.1$, $F=25\%$, $A=50\%$, $L_m=1.0$, $L_o=1.0$, $L_r=1.0$, $FN_m=1.0$ wt%).

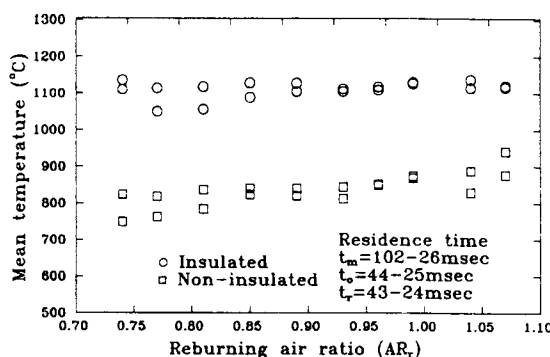


Figure 12. Furnace temperature for reburning zone according to the insulated and non-insulated ($AR_r=1.1$, $F=25\%$, $A=50\%$, $L_m=1.0$, $L_o=1.0$, $L_r=1.0$, $FN_m=1.0$ wt%, $FN_r=0.0$ wt%).

Reburning fuel composition. The properties of the reburning fuel can influence the reburning process directly and also affect its application in practical systems. Figure 11 shows the results when the fuel nitrogen content of the reburning fuel was varied from 0 to 1.5 weight percent nitrogen as NH_3 . Through these experiments main fuel was also propane and the Fuel-N was 1.0 wt%. These data indicate that, as previously reported, the optimum NO reducing zone stoichiometry was approximately 0.85 and that further decreases ultimately resulted in decreased reburning efficiency. These data also show that under optimum reburning conditions, reburning fuel-N has a relatively minor impact on reburning efficiency of NO reduction although it is increase a little with increase fuel-N in the reburning fuel. However if too much reburning fuel is added, exhaust NO_x increase considerably. It is the reason that the temperature of reburning zone is 1,050-1,150 °C as we can see in Figure 12. If the temperature is lower than this experiments, NH_3 addition is effective for NO reduction like SCR (selective catalytic reduction) or SNCR (selective non-catalytic reduction).¹⁷

Thermal Environment. Figure 12 shows temperature distribution according to the reducing zone stoichiometry

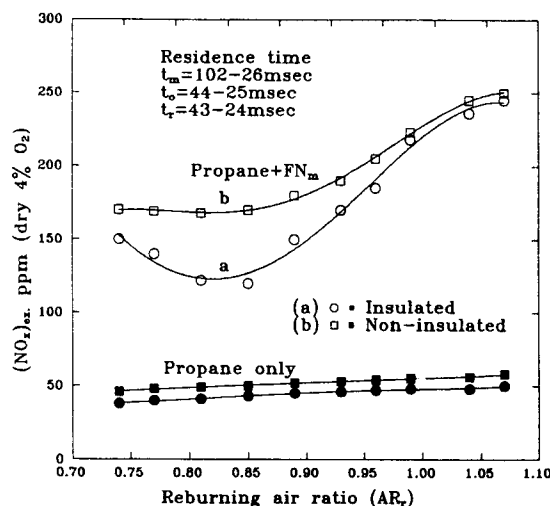


Figure 13. Effect of the temperature of reburning zone on NO_x at exit ($\text{AR}_f=1.1$, $F=25\%$, $A=50\%$, $L_m=1.0$, $L_o=1.0$, $L_r=1.0$, $\text{FN}_m=1.0$ wt%, $\text{FN}_r=0.0$ wt%).

with insulated and non-insulated.

The temperature of reburning zone was 1,050–1,150 °C for insulated case and 750–950 °C for non-insulated case through AR_r .

Figure 13 shows exhaust NO_x concentration on the influence of temperature. NO_x levels are fairly insensitive to the temperature of reburning zone at fuel-lean (i.e., $\text{AR}_r \geq 1.0$). However, under the fuel-rich of reburning zone NO_x reduction was depended on the temperature of reducing zone. Particullary at $\text{AR}_r=0.85$ maximum reduction was achieved with insulated. The data indicate that increasing the temperature significantly increases the amount of NO_x reduction due to an increased rate of N_2 formation. On the other hand, decreasing the temperature of the reburning zone tends to retard the formation of N_2 from the TFN species. It is concluded that the temperature of reburning zone has the greatest influence on NO_x reduction.

Discussion

There is some speculation as to whether or not further reductions in NO_x emission could be achieved by following a rich-lean combustion sequence with another set of rich-lean stage. Figure 1 shows the application of advanced fuel staging which is four stage Rich-Lean-Rich-Lean.

Main combustion zone; Approximately 80–85 percent of the heat is released in this zone under fuel-rich condition. Fuel-N reacts to form intermediates such as NH_3 and HCN in the post-flame gases and that some of this are then oxidized (probably by OH radicals) to form NO . The NO further reacts to form N_2 with the intermediates. NO_x reduction will be achieved by what the rate of destruction of NO can be kept high relative to its rate of formation.

Oxidizing zone; Additional combustion air is added to oxidize any remaining fuel fragments. The remaining reduced N-intermediates (NH_3 and HCN) are either oxidized to NO or reduced to N_2 .

Reducing zone; The reburning fuel (normally 15 to 20 percent of total heat input) is injected upstream of combustion

products to create a fuel-rich, NO reduction zone. NO formed in the main heat release zone reacts with hydrocarbon free radicals during the oxidation of the reburning fuel to produce N-intermediates, and the non-pollutant species, N_2 . In the reducing zone, most of the NO produced in the main combustion zone is effectively reduced to N_2 .

Burnout zone; In the final zone, here air is added to ensure burnout of the reburning fuel. The NH_3 , HCN and NO are either converted to N_2 or NO .

Conclusions

The study on the NO_x emission characteristics was carried out in advanced fuel staged combustion with the following results.

1. NO_x emissions was dependent on the reducing atmosphere of fuel-rich zone regardless of total air ratio. The maximum NO_x reduction was at the AR_r of 0.85.
2. NO_x reduction was effective when burnout air was injected at the point where the reburning zone had been already established.
3. NO_x reduction was dependent upon the temperature of the reducing zone, here was the best effect above 1,000 °C in the reburning zone.
4. In the advanced fuel staging the effects of NO_x reduction was relatively large at the burning of higher Fuel-N concentration in the fuel.
5. Under optimum reburning conditions, fuel nitrogen content has a relatively minor impact on reburning efficiency.
6. The results of this study could be utilized mainly in a design strategy for low NO_x emission from the combustion of high fuel-nitrogen in energy source which can be achieved by advanced fuel staging techniques in large scale facilities.

Nomenclature

- AR : stoichiometric ratio $\{(\text{fuel/air ratio})_{\text{actual}}/(\text{fuel/air ratio})_{\text{sto}}\}$
 FBN : fuel bound nitrogen
 TFN : total fixed nitrogen (NH_3 , HCN and NO)
 D : reactor diameter
 L : injection level referred to as axial dimensionless length (X/D)
 t : residence time
 F : reburning fuel fraction (main fuel/total fuel)
 A : burnout air fraction (oxidizing air/total air)
 FN : fuel nitrogen concentration in the fuel

Subscripts

- t : total
 m : main combustion zone
 o : oxidizing zone
 r : reburning zone
 T : thermal

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Thexylalkoxyborane as Hydroborating Agent for Alkenes and Alkynes

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In order to elucidate the effect of alkoxy substituent in thexylborane and hence establish their usefulness as hydroborating agent, reactions of alkenes and alkynes with thexylalkoxyborane (ThxBHOR; R=Et, *i*-Pr, *i*-Bu, *sec*-Bu, *t*-Bu, Ph) were investigated in detail. The reagents readily hydroborated alkenes and alkynes of various structural types at 25 °C in excellent regioselectivity. The selectivity increases consistently with increasing steric size of alkoxy substituent. Especially, the selectivity achieved by the *sec*-butoxy derivative is comparable to that previously achieved by thexylhaloborane-methyl sulfide (ThxBHX·SMe₂), the most selective hydroborating agent known.

Introduction

Of the most readily available of the monoalkylboranes, thexylborane (2,3-dimethyl-2-butylborane, ThxBH₂)^{1,2} has been demonstrated to be a highly useful reagent for the cyclic hydroboration of dienes.^{3~5} Moreover, the halogen-substituted derivatives of thexylborane, thexylhaloborane-methyl sulfide (ThxBHX·SMe₂; X=Cl, Br, I), are exceptionally valuable reagents for the selective hydroboration of alkenes and alkynes of different structural types.^{6~10} These reagents hydroborate most alkenes and alkynes cleanly with high regio- and stereospecificity to produce isomerically pure thexylalkyl- and thexylalkenylhaloboranes, respectively. These versatile intermediates have been used effectively in organic synthesis.^{8~11} In addition to that, ThxBHX·SMe₂ are also

attractive reducing agents,^{9,10,12~14} especially for the conversion of carboxylic acids and their derivatives to the corresponding aldehydes.^{15,16} These results clearly suggest that the halogen substituent in ThxBH₂ enhances the selectivity dramatically both in reduction and hydroboration reactions.

Accordingly, we decided to extend our investigation to the reaction of alkoxy derivatives of ThxBH₂. We prepared a series of thexylalkoxyborane (ThxBHOR; R=Et *i*-Pr, *i*-Bu, *sec*-Bu, *t*-Bu, Ph) and applied them to the hydroboration of alkenes and alkynes to examine the directive effect, in the hope of better understanding the nature of reagents and of exploring their role in organic synthesis. In this article, we describe in full the results of our study on the hydroboration characteristics of thexylalkoxyborane.