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Reduction of NOx emission from fuel nitrogen in new staged fuelling system(1) (Characteristics of NOx formation & reduction)

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Abstract

The effects of NOx reduction by new staged fuelling system 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 NOx reduction were temperature, reducing stoichiometry(related to main combustion zone stoichiometry, air fraction and reburning fuel fraction) and residence time. The best NOx reduction was observed at the reburning zone stoichiometry of 0.85. In terms of residence time of the reburning zone, NOx reduction was effective when burnout air was injected at the point where the reburning zone has been already established.

1. INTRODUCTION

Nitrogen oxides(NOx) have been recognized as air pollutants for decades due to their effects on human and animal health, damage to vegetation and their roles in producing smog.

Staged combustion has been demonstrated as an effective method for reducing nitrogen oxides emission(L.J.Radak et al.,1982). 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 degree to which the FBN conversion to N_2 is successful is determined by the thermodynamics of the system and the rate of reactions in the fuel rich flame zone (J.M.Levy et al.,1978).

The nitrogeneous compounds in the reducing zone may have two different origins: In the first one of two air staging, they react in rich flames to form intermadiates such as NH3 and HCN in post-flame gases and some of these are then oxidized (probably by OH radicals) to form NO. The NO further reacts by a reaction such as

$$NO + NH_2 \rightarrow N_2 + H_2O$$

If the rate of distruction of NO can be kept high relative to its rate of formation, low fuel-NO will be achieved(C.P.Fenimore,1971). Operation close 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 CH_2 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.(Y.Takahashi et al.,1983) as follows:

$$CnHm + O_2 \rightarrow Cn'Hm'^{*} + CO + H_2O$$
$$NO + Cn'Hm'^{*} \rightarrow Cn''Hm'' + N_2 + H_2O + CO$$
$$NO + Cn'Hm'^{*} \rightarrow Cn''Hm'' + NH_i + H_2O + CO$$

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

As mentioned above, there are many studies about the conventional fuel staged combustion which include three stage Lean-Rich-Lean. However in the case of this method the NOx formation of the primary lean zone is increased by oxidizing atmosphere particularly with higher fuel bound nitrogen fuel.

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 Fig.1. It was the intent of the studies described in this paper to examine the parameters controlling the effectiveness of new staged fuelling system by conducting a series of studies using bench scale reaction with well defined conditions in the NO reduction and the TFN oxidization zones.

2. TECHNOLOGY INTEGRATION

There is some speculation as to whether or not further reductions in NOx emission could be achieved by following a rich-lean combustion sequence with another set of rich-lean stage. Fig.1 shows the application of new staged fuelling system which is four stage Rich-Lean-Rich-Lean.

In 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 some of these are then oxidized(probably by OH radicals) to form NO. The NO further reacts to form N_2 with the intermediates. NOx reduction will be achieved by which the rate of destruction of NO can be kept high relative to its rate of formation.

In oxidizing zone, additional combustion air is added to oxidize any remaining fuel fragments. Most of the remaining N-intermediates(NH3 and HCN) are oxidized to NO.

In reducing zone, the reburning fuel(normally 15 to 20 percent of total heat input) is injected upsteam of combustion products to create a fuel-rich condition, NOx 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 has been reduced to N_2 effectively.

In burnout zone of the final stage, here air is added to ensure burnout of the reburning fuel. The remaining TFN are either converted to N_2 or NO.

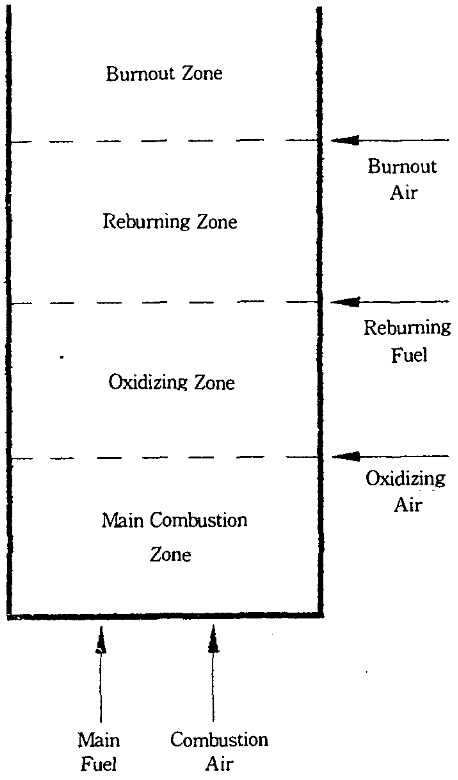

Fig. 1 Schematic of new staged fuelling system

3. APPARATUS

The experimental apparatus shown in Fig.2 is a small-scale test rig. The specification of this test rig is given in Table 1.

3.1 Reactor

The reactor 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 was formed the coaxial diffusion flame and adapted the rim type for the purpose of stabilizing the flame. It was fired within the insulated stainless-steel reactor to minimize heat loss and

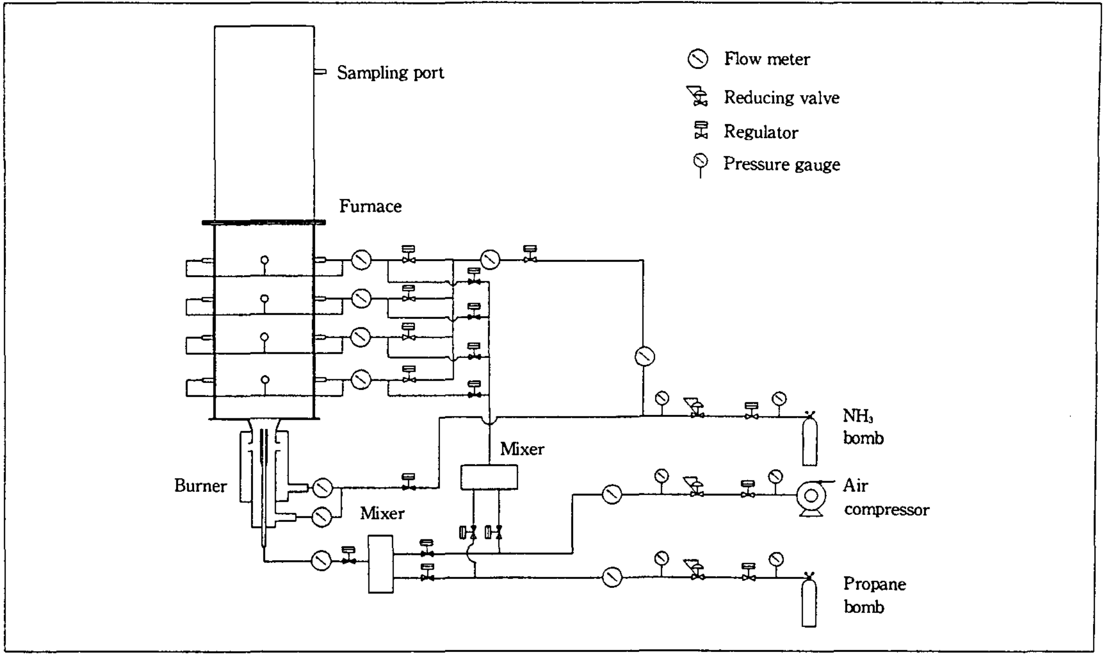

Fig. 2. Schematic of experimental apparatus.

Table 1. Specification of the test rig.

Combustor dimension	Diameter 100mm ×Length 1,200mm
Air(Primary and Stage) Flow Rate	105~134ℓ/min
Inlet Flow Velocity Range	2.5~7.0m/sec
Stage Flow Velocity Range	0~58m/sec
Residence Time Range	4.5sec
Fuel Flow Rage	0.6~4ℓ/min
Fuel Velocity	2~5.5m/s
Swirl number	0.3
Thermal load	$6.6kW_T$
Combustor temperature range	~1300℃

external influences. It has four injection points for reburning fuel and secondary air. At each point four symmetrically spaced radical jets of reburning fuel and secondary 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.

3.2 Gas analysis

The gas species samples were collected using a water-cooled stainless probe. They are filtered and dried before measuring O_2,CO and CO_2 by gas chromatography, and the measurement of NOx is carried out using a chemiluminecent analyzer. HCN and NH_3 were measured by an ion-electrode method(M.Sadakata et al.,1981). Since NH_3 and HCN are easily absorbed by water, all of the sampling line was heated up to between 100℃ and 150℃ 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 0.1mm) thermocouple. The results were corrected for radiation error.

3.3 Test condition

The approach taken in the present study is to know the NOx reduction of new staged fuelling system under well controlled conditions. This is accomplished by the contruction of a reactor which provided ready access for several diagnostic systems. The main and reburning fuel is used the propane laden with ammonia as fuel bound nitrogen, which is fed at a rate of 4 l/min.

4. EXPERIMENTAL

Test were conducted such that the SRm's was changed from 0.5 to 1.4 while the SR_t was kept constant throughout each experiment. The effect of NOx reduction on new staged fuelling system was to be investigated about various parameters which were temperature, stoichiometry, residence time and reburning fuel composition.

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 than 1 hour and covered a range of stoichiometric ratio.

5. 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 new staged fuelling system.

Fig.3 shows the variation of exhaust gas concentration of no-stage combustion according to stoichiometric ratio(SR). NOx concentration at SR of 1.1 is a maximum as 348 ppm for the flame of propane with Fuel-N and 40 ppm for the propane only. Therefore the 90 percentage of the propane flame with fuel-N is fuel-NOx. As SR increases from 1.1 to 1.4, Absolute fuel-NOx concentration was increased with lower temperature by excess air although it seems to be decreased by dilution effects of excess air. For lower SR than 1.0, NOx concentration is decreased drastically and N-intermediates(HCN, NH_3) is increased gradually because of lower gas temperature and oxygen concentration. These results show that most of the nitrogen in the fuel is converted with fuel-lean condition. However because of NOx reduction at fuel-rich condition it can be applied to the staged fuel converson system when the stoichiometry of reducing zone maintains fuel-rich.

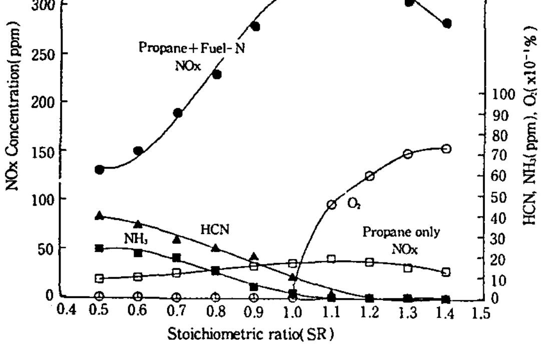

Fig. 3 Exhaust gas concentration with no-staging. (Fuel-N=1.0 wt%)

Figs.4, 5, 6 show the variation of gas concentration according to the residence time at SR_t of 1.1 on new staged fuelling system.

NOx, NH_3, HCN, TFN and N_2 levels are shown in Fig.4 with $SR_m=0.8$,$SR_o=1.13$ and $SR_r=0.85$. 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 as Fuel-N decreases drastically at near the burner and does not exhibit any strong peak. The total sum of all of the fixed nitrogen species, which have the potential of being converted to NO in the burnout zone, has a sharp peak as 300ppm at 0.75 sec followed by a rapid decay process in the reburning zone. N_2 concentration increases with the increase of TFN in the reburning zone. The reason which increased TFN gradually in the main combustion, is that at the fuel-rich atmosphere of main combustion zone Fuel-N is converted to N-intermediates or N_2 like substoichiometry in Fig. 3. Fenimore(C.P.Fenimore, 1972) also observed the passage of a relative N-intermediate through flames near the fuel-rich limit. After this region the NOx emission increased rapidly because combustion products are mixed with the oxygen of combustion air. However the reburning fuel is injected downstream of the oxidizing zone to create a fuel-rich, NOx 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 NH_3, and non-pollutant species, N_2. In the reburning zone, most of the NO produced in the oxidizing zone is effectively reduced to N_2. In the burnout zone, additional combustion air is added to oxidize any remaining fuel fragments and produce overall fuel-lean conditions. The remaining reduced nitrogen species(NH_3 and HCN) are either oxidized to NO or reduced to N_2. Successful application of the staging concept requires that the reduction in concentration of the TFN 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 Zeldovich NO formation rates are appreciable(1800° K).

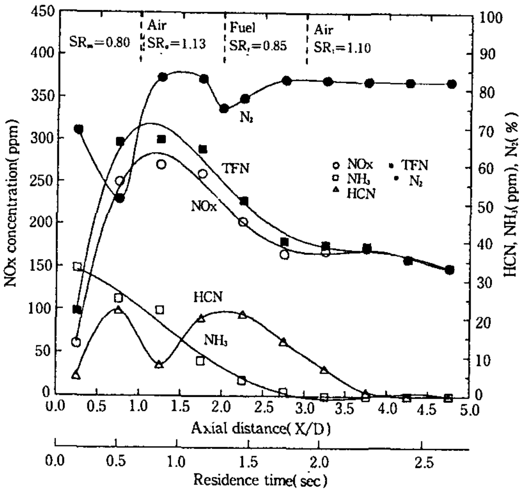

Fig. 4. Nitrogen species profile along the axis with $SR_r=0.85$($F_r=25\%$ $F_a=50\%$ $L_a=1.0$ $L_f=1.0$ $L_{aa}=1.0$ Fuel-N=1.0wt%)

NOx, NH_3 and HCN levels is shown in Fig.5 with $SR_m=0.6$, $SR_o=1.03$ and $SR_r=0.77$. The rapid NOx production at 1.2sec is a peak level of 290ppm characteristic of fuel-lean burning because fuel bound nitrogen and N-intermediates which formed in the main combustion zone react with the oxygen of secondary air as can be known by decreasing the HCN and NH3 in the oxdizing atmosphere. In the reburning zone, a part of the NO produced in the main combustion zone is reduced to N_2. However because of the increase of N-intermediates in $SR_r=0.77$, TFN is decreased more gradually in comparison with $SR_r=0.85$ in Fig.4.

NOx, NH_3 and HCN levels is shown in Fig.6 with $SR_m=1.2$, $SR_o=1.33$ and $SR_r=0.99$. The rapid NOx production was achieved with oxidizing atmosphere ($SR_m=1.2$) in the main combustion zone. In the earlier study(JSME,1988) at the oxdizing atmosphere of main combustion zone NOx emission increases drastically near the burner. Corresponding NH_3 and HCN levels are low in the highly oxidizing main combustion zone. It may be concluded from the above results that NOx emission for new staged fuelling system is decreased sharply in the condition of $SR_m=0.8$ and $SR_r=0.85$.

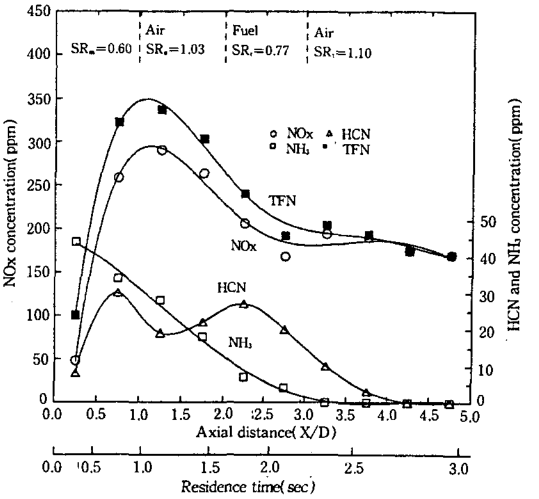

Fig. 5. Nitrogen species profiles along the axis with $SR_r=0.77$.($F_r=25\%$ $F_a=50\%$ $L_a=1.0$ $L_f=1.0$ $L_{aa}=1.0$ Fuel-N=1.0wt%)

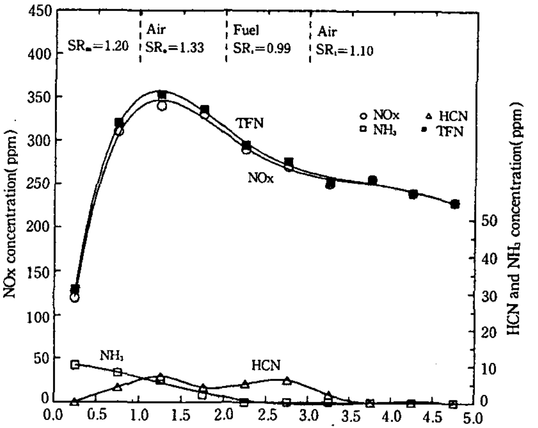

Fig. 6. Nitrogen species profiles along the axis with $SR_r=0.99$.($F_r=25\%$ $F_a=50\%$ $L_a=1.0$ $L_f=1.0$ $L_{aa}=1.0$ Fuel-N=1.0wt%)

Fig.7 shows the profiles of oxygen concentration according to the residence time of the reburning zone. When t_r is 1.11sec, the oxidizing atmosphere prevails but when t_r is 0.56sec, the reducing atmosphere prevails.

Fig.8 shows the variation of NOx concentration according to SR_r.

For propane-air flames with no fuel-N added, little thermal-NOx decreased as SR_t increased from 1.1 to 1.4 because maximum temperature was decreased from 1,163 ℃ at SR_t of 1.1 to 1,065 ℃ at SRt of 1.4. Thermal-NOx emission in this reactor is very low because of its low flame-temperature. Through this study, combustion was achieved lower than the temperature(1,800°K) explained in terms of thermal-NO formation, i.e. Zeldovich kinetics(Irvin Glassman,1987).

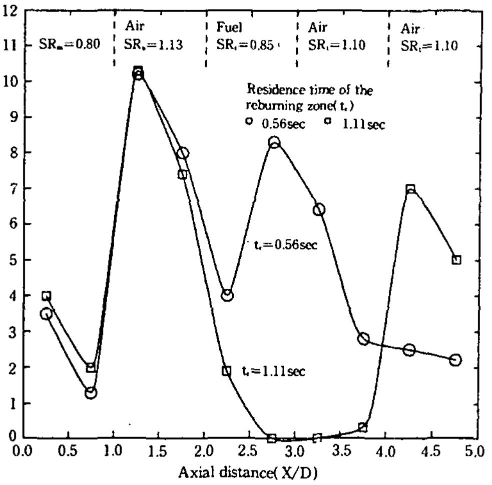

Fig. 7. Profiles of oxygen concentration according to residence time.(F_r=25% F_a=50% L_a=1.0 L_f=1.0 L_{aa}=1.0 Fuel-N=1.0wt%)

For propane-air flames with fuel-N added, the NOx profiles according to SR_t are almost similar although they increase a little. Because the increasing of SR_t means the increasing of stoichiometric ratio in oxidizing and burnout zone, little fuel-NOx is increased by oxidizing it with Fuel-N and so it is almost independent of SR_t. The required stoichiometry for optimization of the NOx reducing zone is an important patameter 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 SR_r decreases gradually, the exhaust NOx is reduced drastically until the optimum stoichiometry($SR_r \simeq 0.85$) regardless of SR_t. The percentage NOx reduction was achieved 70 percent relative to baseline levels at SR_t of 1.1. Further decreases in SR_r cause an increase in the exhaust NOx. The purpose of the NOx reducing zone is to react the nitric oxide leaving the oxidizing zone with hydrocarbon radicals(such as CH, CH_2, CH_3) provided by the reburning fuel. In additon, there appears to be considerable interconversion of nitrogen among different N-intermediates. At SR_r less than 0.85, NH_3 and HCN formation becomes significant as can be seen in Fig. 5. Further these data demonstrate that as reburning zone stoichiometry is reduced, the summation of the fixed nitrogen species increases dramatically. From these result it could be concluded that the best NOx reduction is at SR_r of 0.85 and reburning zone stoichimetry is an important patameter regardless of SR_t. The temperature in the reburning zone is 1000℃ -1140 ℃ regardless of reburning stoichiometric ratio as in Fig. 9. Nitrogen reduction by ammonia also is effective only in a narrow temperature range about T~1250 K (Irvin Glassman, 1987). Throughout this study, the profiles of the temperature are similar to those described above.

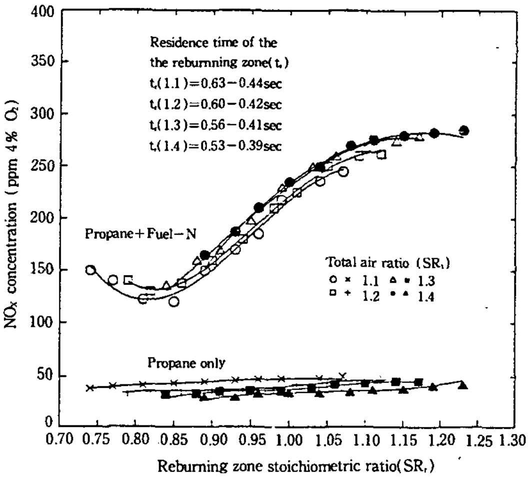

Fig. 8 Effect of reactant stoichiomtry on NOx at exit.(F_r=25% F_a=50% L_a=1.0 L_f=1.0 L_{aa} =1.0 Fuel-N=1.0wt%)

Fig. 10 shows the variation of CO, CO_2 concentrations at exit according to the SR_r with SR_t=1.1. CO emission is an index of combustion efficiency. CO emission 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 NOx emission control, CO emission decreased at a minimum. CO_2 concentration was about 11 %.

Throughout the experiments, the profiles of exhaust gas concentrations are similar to those described above.

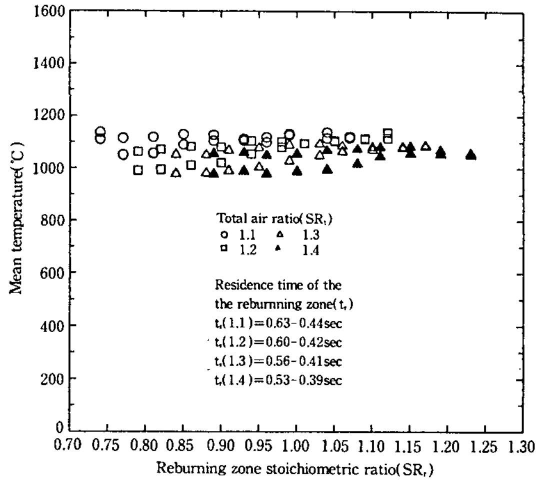

Fig. 9. Reburning zone temperature according to reactant stoichometry.($F_r=25\%$ $F_a=50\%$ $L_a=1.0$ $L_f=1.0$ $L_{aa}=1.0$ Fuel-N=1.0wt%)

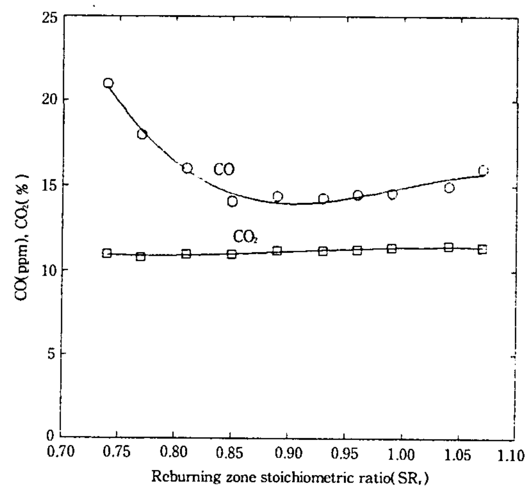

Fig. 10. CO and CO_2 concentration at exit. ($F_r=25\%$ $F_a=50\%$ $L_a=1.0$ $L_f=1.0$ $L_{aa}=1.0$ Fuel-N=1.0wt%)

6. CONCLUSIONS

The study on the NOx emission characteristics was carried out in a gas flame with new staged fuelling system as the following results.

1) NOx emissions are dependent on the reducing atmosphere of fuel-rich zone regardless of total air ratio. The maximum NOx reduction is at the SR_r of 0.85.
2) NOx reduction is effective when burnout air is injected at the point where the reburning zone is already established.
3) As the SR_r was increased to the optimum level for NOx emission control, CO emissions decreased to a minimum.

NOMENCLATURE

SR stoichiometric ratio
FBN fuel bound nitrogen
TFN total fixed nitrogen(NOx+NH_3+HCN)
X axial distance
D reactor diameter
L injection level referred to as axial dimensionless length(X/D)
t residence time
Fr reburning fuel fraction(main fuel/total fuel)
Fa air fraction(oxidizing air/total air)
Fuel-N fuel nitrogen concentration in the fuel
Subscripts
t total
m main combustion zone
o oxidizing zone
r reburning zone
a secondary air
f reburning fuel
aa burnout air
T thermal

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