

## NITROGEN OXIDE REBURNING WITH HYDROCARBON FUELS

Thomas E. Burch, Franz R. Tillman, Wei-Yin Chen\*, and Thomas W. Lester

*Department of Mechanical Engineering, Louisiana State University, Baton Rouge, LA 70803*

*\*Corresponding Author; Present Address: Department of Chemical Engineering, University of Mississippi, University, Mississippi 38677*

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### Introduction:

Reburning (or fuel staged combustion) is a furnace  $\text{NO}_x$  control process that utilizes the reduction powers of hydrocarbons. This concept and the term reburning were first proposed by Wendt, et al. (1973). However, reburning was not established as a practical  $\text{NO}_x$  reducing method until Takahashi, et al. (1983) reported greater than 50% reduction of NO in tests at Mitsubishi Heavy Industries. Reburning comprises three zones in the combustion process. The primary zone is the main heat release zone in which approximately 80% of the fuel is burned in a fuel lean (SR = 1.1) environment. This is followed by a reburning zone where additional fuel is added to give an overall fuel rich stoichiometry (ca. SR = 0.9). Finally additional air is provided in the burnout zone to complete the combustion process by burning off residual hydrocarbons in a fuel lean environment.

This study addresses the mechanisms of NO reduction in pulverized coal combustion using reburning. The interactions between NO and hydrocarbon constituents in the fuel, and the fate of fuel nitrogen are the focal points of this research. Nitrogen oxide reduction and formation mechanisms in reburning stage are investigated with a laboratory scale flow reactor. Feed to the reactor includes simulated flue gas and reburning fuels (methane, benzene, hexane, coal, and lignite). This paper discusses the implications of nitrogen product distribution as functions of second stage stoichiometry and reburning fuel type. In addition, a unique GC/MS technique established for the systematic analysis of flue gas will be presented.

### Experimental:

The experiments reported here were carried out in a ceramic flow reactor (Figure 1) with a simulated flue gas consisting of 16.8%  $\text{CO}_2$ , 1.95%  $\text{O}_2$ , and 0.1% NO in a helium base. These concentrations of  $\text{CO}_2$ ,  $\text{O}_2$ , and NO were chosen to be consistent with those of a coal primary flame operated at a stoichiometric ratio of 1.1. Helium, instead of nitrogen, was used as the base gas to minimize heating time due to its low heat capacity.

The flow reactor used for this research was an alumina tube (Coors Ceramics Co.) with an inside diameter of 0.75 in. and an overall length of 24 in. The central portion of the reactor tube was enclosed in a 12 in. long electrically heated furnace (Lindberg Model 55035) which provided tube temperatures up to 1150°C.

For experiments using coal as a reburning fuel, the delivery system was modified to incorporate a laboratory scale coal feeder shown schematically in Figure 2. Details of this device have been reported elsewhere (Burch, et al. 1990). The coal feeder required part of the gas flow (usually helium) to be diverted through the coal feeder for use as carrier gas.

The sampling train consisted of 0.25 in stainless steel transfer lines and switching manifold with stainless steel valves. Transfer lines from the reactor tube exit to the impinger were heat traced to prevent absorption of HCN and  $\text{NH}_3$ . The effluent was desiccated with anhydrous calcium sulfate before transfer to the instrument package through 0.25 in teflon tubing. For coal experiments, the sampling train was modified to allow the gaseous products (and particulate matter) to pass straight through the end of the reactor tube into a paper filter before entering the transfer lines. The filter was enclosed in a glass housing and heated to 100°C. Recovery tests showed no loss of HCN or  $\text{NH}_3$  in the filter. A 10  $\mu\text{m}$  filter was also added upstream of the desiccant dryer for coal experiments. The flow reactor was maintained near atmospheric pressure by providing an atmospheric vent downstream of the instrument package and monitoring the supply gas pressure in the mixing chamber.

HCN and  $\text{NH}_3$  were collected by diverting the reactor effluent through a straight tube impinger filled with 0.5 L of 0.1N  $\text{HNO}_3$  aqueous solution for a specified time interval. The captured solutions were pH adjusted using NaOH

and analyzed for CN- and dissolved ammonia with specific ion electrodes (Orion Research). Poisoning of the cyanide electrode by sulfur ions from coal combustion was prevented by adding an aqueous solution of  $PbNO_3$  prior to adding the NaOH. Sulfide ions were precipitated as  $PbS$ . Recovery of HCN and  $NH_3$  by this method was tested using known standards and found to be near quantitative for  $NH_3$  but only 70% for HCN. Thus  $NH_3$  values have been presented as measured while HCN values reported have been corrected for collection efficiency.

Qualitative analysis or separation of nitrogenous species were also performed by GC/MS. Samples of the reactive effluent were captured in 300  $cm^3$  stainless steel containers. To eliminate contamination from past runs the containers were heated under vacuum between runs to remove HCN and  $NH_3$  absorbed into the walls.

Two chromatographic columns were used for separation of the nitrogen compounds.  $N_2$  and NO were effectively separated from other fixed gases on a 20 ft x 1/8 in S.S. Hayesep D<sub>3</sub> column (Hayesep separations) at 25°C isothermal. Separation of  $NH_3$  and HCN was accomplished using an 8 ft x 1/8 in. S.S. Hayesep C column operated at 80°C for  $NH_3$  and 120°C for HCN. Due to active sites on the column, low concentrations of these specifics (less than 200 ppm) required several saturation injections and isothermal conditions to give quantifiable mass peaks. Lower concentrations of  $NH_3$  and HCN (less than 75 ppm) were analyzed by "loading" the column with repeated injection onto a cold column (25°C). The oven temperature was then rapidly raised to the desired operating temperature to facilitate elution. This procedure was repeated until the yields of the HCN and  $NH_3$  were stabilized, signifying that active sites were filled with species from the current sample.

GC/MS samples were injected via evaluated and heated static injection loops. For fixed gas analysis, a 10  $cm^3$  S.S. loop was used. For HCN and  $NH_3$  analysis a 40  $cm^3$  S.S. loop was used to help overcome low concentrations and active column sites.

## Results and Discussion:

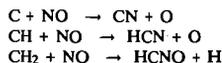
### - Gaseous Fuels Results

Reburning experiments were conducted for methane, hexane and benzene at a reburning temperature of 1100°C and an estimated reaction time of 0.2 seconds. The stoichiometry for these tests was varied from SR = 0.7 to 1.0. The resulting TFN (total fixed nitrogen; ie, all nitrogen species except  $N_2$ ) speciation profiles are illustrated in cumulative fashion by the curves in Figure 3 through 5.

The minimum TFN for each of these fuels occurred near SR = 0.95 under these conditions. However, the minimum value attained and the sensitivity to stoichiometry were found to be considerably different for the three fuels. Also, the TFN speciation in the neighborhood of the minimum TFN was radically different.

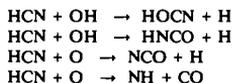
For methane the dominant fixed nitrogen species at the optimum stoichiometry was NO which accounted for more than 85% of the total. In benzene reburning, the contribution of NO at the optimum stoichiometry was only 2% of the total with HCN making up 75%. Hexane fell in between these two extremes with NO and HCN contributions of 33% and 60% respectively. It is interesting to note that hexane exhibited the lowest TFN.

Employing the mechanisms and sensitivity analysis of Miller and Bowman (1989) along with calculations conducted by Chen et al. (1989) it seems reasonable to view reburning as possessing two major kinetic barriers. The first barrier is the conversion of NO to HCN by combination with various hydrocarbon fragments such as



The accepted rate constants for these reactions are all within roughly one order of magnitude so the dominant mechanism in the conversion of NO to HCN is strongly dependent on the relative concentrations of the reducing species produced. Regardless of which mechanism dominates, there is general agreement that the end product is HCN, whether formed directly or by rapid conversion of intermediates such as CN.

The second major kinetic obstacle appears to be oxidation of HCN via one of the following reactions:



Having accomplished this step the subsequent conversion to N atoms is rapid. N atoms are then recycled to form NO or react with NO to form N<sub>2</sub>.

Using this two barrier concept many of the salient features of reburning can be interpreted. First the concentration and longevity of reducing species at near stoichiometric conditions is so low that substantial quantities of the initial NO remains unreacted. As the stoichiometry is shifted to more fuel rich conditions, competition from other oxidizing species decreases allowing concentrations of reducing species to build and react with NO. Thus at richer stoichiometries, most of the NO is converted to HCN. Actually the concentration of reducing species appears to peak somewhere around SR = 0.9, then slowly declines as the stoichiometry becomes more fuel rich. However, the general trend described above appears valid.

The concentration of oxidizing species needed to overcome the second barrier follows an opposite trend. At lean stoichiometries the populations of O and OH are high, effectively converting most form HCN to subsequent species. As the stoichiometry becomes richer the concentration of oxidizing species is depleted by reaction with abundant reducing species.

Thus, in leaner stoichiometries, the dominant kinetic barrier appears to be the initial reduction of NO whereas in rich stoichiometries the conversion of HCN to subsequent species is the major obstacle. The optimum stoichiometry is then defined by a compromise between these processes. Based on this admittedly simplistic argument the behaviour exhibited in Figures 3 through 5 can be interpreted.

For methane, the fact that the minimum TFN contains primarily NO indicates that reduction of NO to HCN is the limiting factor. The carbon to hydrogen ratio of methane (1 to 4) may not provide enough of the appropriate reducing species to effectively convert NO to HCN until the stoichiometry becomes too fuel rich to sustain good populations of O and OH.

Although any comments on the breakup of hexane and benzene is somewhat speculative, one might expect these fuels which are more carbon rich to produce CH<sub>i</sub> (i > 0, 1, 2) fragments in greater numbers at stoichiometries lean enough to still support substantial O and OH populations. The hexane curves (Figure 4) seem to follow this reasoning in that more of the NO has apparently been converted to HCN at SR = 0.95 where a substantial quantity of the HCN produced was converted to subsequent species leading to N<sub>2</sub>.

Benzene shown in Figure 5, continued the trend of increasing reduction of NO to HCN as the carbon content of the fuel increased. However, the expected attending conversion of HCN to N<sub>2</sub> at this relatively lean stoichiometry was not observed. Perhaps the benzene oxidation mechanism is such that O and OH species are consumed too rapidly (or not produced at all) to allow for the conversion of HCN.

The timing of peak concentrations of important species is also critical. Since the conversion of HCN to N<sub>2</sub> by necessity succeeds the reduction of NO to HCN, high populations of NO reducing species occurring after O and OH have been depleted serve to reduce NO but not TFN.

One final observation is that the true optimum stoichiometry for benzene (or methane) may not have been found. The high levels of HCN at SR = 0.95 would seem to suggest that a leaner stoichiometry might yield a better conversion of HCN to N<sub>2</sub> without seriously impairing the reduction of NO to HCN. Similarly, the high NO and low HCN exhibited by methane at SR = 0.95 would indicate a slightly richer stoichiometry might improve overall TFN levels.

#### *Coal Results*

Reburning experiments were conducted for a Pittsburgh #8 bituminous coal and a North Dakota lignite with reburning conditions identical to those used for gaseous fuels. The analyses of the two coals used are given in Table 1.

Each of the coals were sieved between 200 and 270 mesh to provide a uniform particle size for feeding and to eliminate particle size considerations in comparison of results.

Char samples were collected from reburning experiments ranging from  $SR = 0.7$  to  $SR = 1.0$ . Analysis of these samples for each coal showed no more than a statistical variation in nitrogen retained in the char. On average, lignite char retained 50% of the nitrogen contained in the coal whereas bituminous char contained 58% of the original nitrogen. Apparently, reburning with these conditions involves primary devolatilization with little or no char oxidation taking place. Average data were used to determine char nitrogen with ash as a tracer.

The cumulative TFN speciation for the Pittsburgh #8 coal is shown in Figure 6. The most notable feature of this graph is that the minimum gas phase TFN occurs at  $SR2 = 0.85$  whereas for gaseous fuels  $SR = 0.95$  produced minimum TFN. This is reasonable if reburning is considered to be controlled primarily by homogeneous gas phase reactions. Since part of the hydrogen were retained in the solid phase as char, the gas phase stoichiometry was somewhat leaner than the overall stoichiometry.

The gas phase TFN exhibited by the Pittsburgh #8 coal appears very similar to a stretched version of the hexane distribution both in minimum TFN value and speculation. However, the retained char nitrogen added considerably to the fixed nitrogen pool and accounted for more than 65% of the total at  $SR = 0.85$ .

Lignite reburning produced more novel results as shown in Figure 7. The minimum TFN for lignite occurred at  $SR = 0.9$  owing partially to higher volatility of combustible species. Surprisingly, reduction of NO was nearly complete for stoichiometries below  $SR = 0.85$  achieving levels below 1 ppm. Another unusual feature is that for all stoichiometries below  $SR = 0.90$  the gas phase TFN is totally dominated by  $NH_3$ . HCN levels never exceeded 17 ppm at any stoichiometry.

Although fuel rich combustion and pyrolysis experiments reported in the literature (eg. Chen, et al., 1982) have shown high levels of  $NH_3$  from lignites the results presented here differ in that much of the gas phase nitrogen in these experiments did not originate in the coal. The extremely low NO and HCN levels (normally the dominant species in reburning) suggest that most of the original NO has been converted to either  $NH_3$  or  $N_2$ . These peculiar results spanned an effort to isolate the reason for this behavior and to see if the low NO, low HCN, and high  $NH_3$  levels were related.

Heterogeneous reactions of NO are usually discounted in reburning as too slow to be of any consequence. However, a suitable gas phase mechanism could not be found so the search was directed toward heterogeneous mechanisms. The following sequence of tests was conducted and the corresponding results given.

The effect of char addition rate on surviving NO levels with varying gas composition was studied. The char was collected from lignite reburning at  $SR = 0.85$ . First, the standard gas composition used for other reburning experiments (i.e. 16.8%  $CO_2$ , 1.95%  $O_2$ , 1000 ppm NO, balance He) was used. For reference a char feed rate of 0.029 gm/min corresponds to the char loading found in lignite reburning at  $SR = 0.9$ . The results are shown in Curve 1 of Figure 8. As the char feed rate was increased, the surviving NO levels gradually decreased and then abruptly fell to less than 10 ppm. This precipitation decline was accompanied by the disappearance of measurable  $O_2$  in the reactor effluent. This suggested competition for active sites on the char surface.

The results shown in Curve 2 of Figure 8 were obtained by replacing the  $O_2$  in the feed gas with helium so that  $CO_2$  remained the only oxidizer competing with NO for active sites. The elimination of  $O_2$  had a profound effect in that very low surviving NO levels were measured with significantly reduced char feed rates. However, some competition for active sites persisted as evidenced by the reduction of  $CO_2$  to CO when char was fed.

Finally, the effect of char on surviving NO with only NO and He in the feed gas is shown in Curve 3 of Figure 8. Eliminating the  $CO_2$  from the feed gas further reduced the required char feed rate to the point that any char feed resulted in almost total elimination of NO from the reactor effluent.

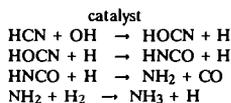
In all of the above tests only low levels of HCN and  $NH_3$  were formed because of the absence of available hydrogen. Also, the reaction was almost certainly heterogeneous instead of surface catalyzed gas phase since gas phase reactants were almost non-existent. DeSoete (1980) gives an excellent review of possible mechanisms.

Next attention was turned to the unusually high production of  $\text{NH}_3$  in lignite reburning. Again heterogeneous effects were suspected. To confirm this, a methane reburning experiment was conducted at  $\text{SR} = 0.9$  with char addition at a rate of approximately  $0.0194 \text{ gm/min}$ . The results of this experiment (shown in Table 2) were very similar to those from lignite reburning. The only difference of note was the lower  $\text{NO}$  level produced by methane/char reburning because of the richer gas phase stoichiometry.

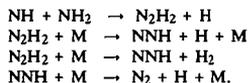
Next, lignite ash was produced by burning char in excess  $\text{O}_2$  at  $1100^\circ\text{C}$  and fed with methane at  $\text{SR} = 0.9$ . Again, high levels of  $\text{NH}_3$  were produced as shown in Table 2. However, in this experiment the surviving  $\text{NO}$  level was similar to that when reburning with methane alone. Also, the  $\text{NH}_3$  level was almost twice that of methane/char reburning.

Since the ash contained very little carbon, the direct heterogeneous reduction of  $\text{NO}$  on carbon was eliminated. This caused more of the nitrogen to be converted to  $\text{HCN}$  as in reburning with methane alone.

In the final experiments, (shown in Table 2)  $\text{NO}$  was replaced with approximately 500 ppm of  $\text{HCN}$  in methane/char reburning. Again the final TFN distribution was weighted heavily in favor of  $\text{NH}_3$ . Although not conclusive, these tests strongly indicate that increased  $\text{NH}_3$  production with lignite reburning was the result of  $\text{HCN}$  conversion in an ash catalyzed reaction. However, direct conversion by addition of  $\text{H}_2$  would seem unlikely. A mechanism such as the sequence



would be more plausible. In the mechanism, some of the  $\text{HCN}$  converted to  $\text{NH}_2$  would be subsequently converted to  $\text{N}_2$  via



Thus the lower total fixed nitrogen found in methane/ash versus methane alone would be accounted for.

The usually strong heterogeneous and/or catalytic effects observed with lignite char are particularly interesting in light of the apparent absence of such effects with bituminous char. The reason for this disparity is not known and may be due to differences in the nature of the chars.

The lignite ash (PSOC 1507) composition as reported by the Pennsylvania State University Coal Research Section was unusually rich in calcium oxide (23.2%), barium (6570 ppm), and strontium (4900 ppm). On the basis of concentrations alone, these seem to be the most likely candidates for catalysts.

The heterogeneous reduction of  $\text{NO}$  is most likely due to the large surface area of the very porous and friable lignite char. However, this may also be a catalytic effect. Several authors including Walker et al. (1968) have observed enhancement of char oxidation rates when the chars were impregnated with various transition metal compounds.

## Conclusions

The choice of fuels has a very definite impact on the TFN speciation and minimum TFN achievable in reburning. The estimated  $\text{NO}$  concentrations after burnout for the fuels tested in this work can be calculated based on 80% conversion of gas phase fixed nitrogen and 20% conversion of char nitrogen to  $\text{NO}$ . From these calculations, it would appear that the lignite has the greatest potential in spite of its fuel bound nitrogen.

The strong heterogeneous/catalytic activity of the lignite char could have important consequences for practical reburning enhancement. It appears that lignite char at least partially removes the current kinetic barriers in reburning

by directly converting NO to N<sub>2</sub> and by converting HCN to other nitrogenous species that are more readily converted to N<sub>2</sub>.

Addition of lignite char in methane, reburning reduced gas phase TFN by 71%. If the char could be produced with low nitrogen constant or used in smaller quantities without adversely affecting the desirable characteristics, overall TFN could be reduced to extremely low levels. Even the simple addition of lignite ash in methane reburning reduced TFN levels by 39% over methane alone. Although temperature, scale up, and mixing effects need to be studied and may impact the utility of this scheme, enhanced reburning by injection of suitable char/ash may show some promise.

### Acknowledgements

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Table 1. Analysis of Coals

	Pittsburgh #8, Bituminous	North Dakota Lignite (PSOC 1507)
Moisture*	2.02	33.57
Carbon	70.48	62.61
Hydrogen	4.66	4.41
Oxygen (Diff)	8.53	18.23
Nitrogen	1.44	0.83
Sulfur	3.35	1.43
Ash	11.54	12.49
Vol. Matter	33.25	40.77
Fixed Carbon	55.21	46.75

\*Moisture is reported on an as received basis all other results are on a dry basis.

Table 2. Total Fixed Nitrogen Speciation with Addition of Lignite Char/Ash.

Reburning Fuel	CH <sub>4</sub>	Lignite	CH <sub>4</sub> /char	CH <sub>4</sub> /ash	CH <sub>4</sub> /char
N in Feed	NO	NO	NO	NO	HCN
Concentration, ppm	1000	1000	1000	1000	500
Effluent Species					
NO, ppm	90	32	5	70	1
HCN, ppm	308	12	9	10	12
NH <sub>3</sub> , ppm	105	135	130	227	51

Gas phase SR = 0.9 for all tests.

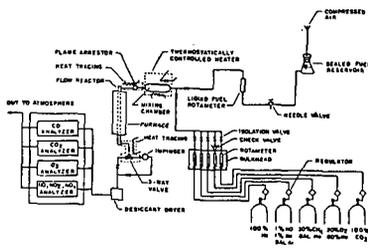


Figure 1. Schematic of experimental facility.

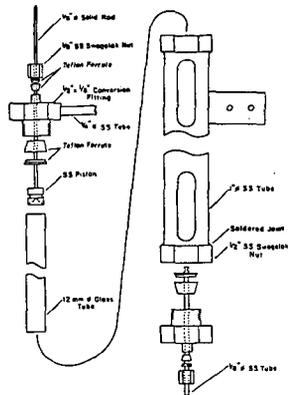


Figure 2. Exploded view of coal feeder assembly.

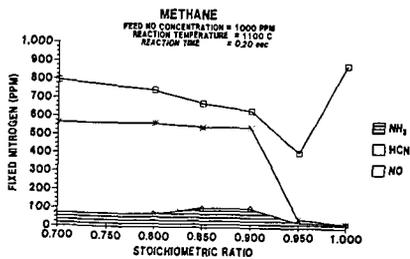


Figure 3. Cumulative total fixed nitrogen for methane reburning.

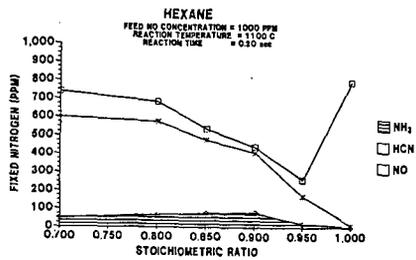


Figure 4. Cumulative total fixed nitrogen for hexane reburning.

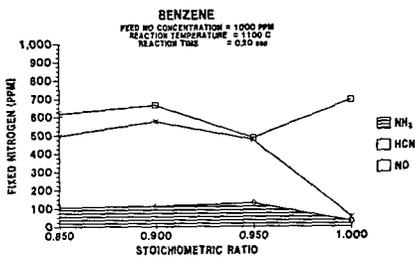


Figure 5. Cumulative total fixed nitrogen for benzene reburning.

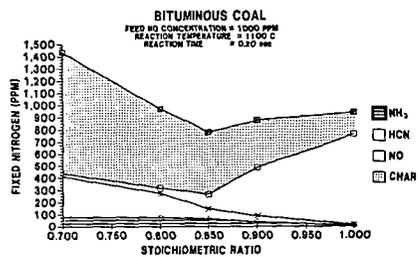


Figure 6. Cumulative total fixed nitrogen for reburning with Pittsburgh #8 bituminous coal.

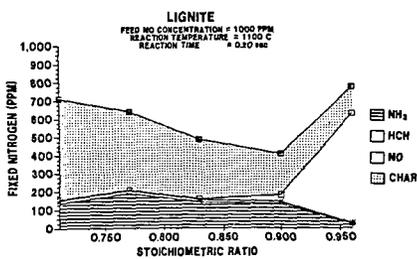


Figure 7. Cumulative total fixed nitrogen for reburning with Zap, North Dakota lignite.

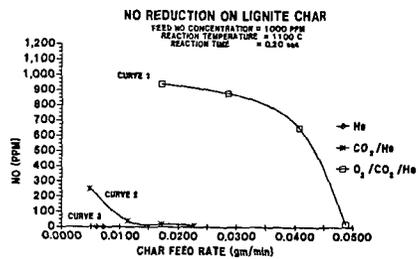


Figure 8. Influence of gas composition on heterogeneous reduction of NO with lignite char.