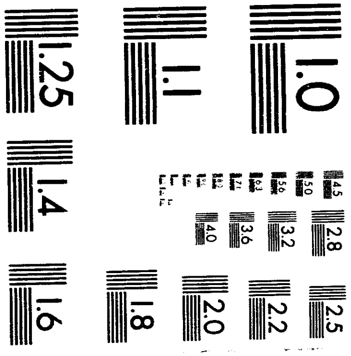
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ROLE OF CHAR DURING REBURNING OF NITROGEN OXIDES

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ABSTRACT

Nitrogen oxide is a major air pollutant generated during coal combustion. In the last few years, we have been investigating various mechanisms for the in-furnace reduction of nitrogen oxide under the support of U.S. Department of Energy (Chen *et al.*, 1991) and the Mississippi Mineral Resources Institute (Chen *et al.*, 1992). It was discovered that nitrogen oxide can be effectively reduced over lignite char surface in a fuel rich environment called "reburning." These conclusions have been drawn from tests on reactors of two different scales and two lignites: one from Mississippi and the other from North Dakota.

Reburning is a three-stage combustion process designed for NO reduction. The primary combustion zone produces more than 80% of the total energy output similar to a conventional furnace. A small amount of reburning fuel is introduced into the second stage where the majority of NO is chemically reduced to nitrogen. The unburned fuel is then combusted in the third stage by introducing additional air.

Customarily, coal and lignite have not been considered viable reburning fuels for a number of reasons. NO reduction through homogeneous gas phase mechanisms is generally believed more important than the heterogeneous NO reduction on char; and coal devolatilization in the fuel rich environment generates only about 50% of the volatile hydrocarbon radicals than gaseous hydrocarbons under the same fuel-to-oxidant stoichiometry. In addition, the fuel nitrogen could result in additional nitrogen oxide emissions in the burnout stage. What has not been anticipated is the highly active nature of lignite char surface. First, it has been demonstrated in the literature that lignite char can be gasified by nitrogen oxide; second, the minerals in lignite char can catalyze the CO + NO and gasification reaction; and third, lignite char has a highly porous structure which is desirable for gas/solid reactions. The unique NO activity on char surface is expected to

benefit the utilities which are involved in coal combustion and have to meet the stringent Clean Air Act Amendments of 1990.

This program is aimed at a better understanding of the chemical and physical mechanisms involved in the reburning with chars. Char gasification rates will be measured with and without the presence of CO. Further, the rate of the char catalyzed CO+NO reaction will also be measured. Experiments have been conducted with a flow reactor which simulats the reburning stage. One bituminous coal and two lignites, one from North Dakota and the other from Mississippi, are used in these tasks. A unique component of this program is the use of the fractal concept in the estimations of these gas/solid reaction rates. The proposed program is designed to investigate the relative importance of these two reactions (char gasification and ash catalyzed CO+NO reactions) under reburning conditions.

Research completed in the first quarter includes: reassembly of the flow reactor, fabrication of a char/ash collection unit, sample preparation, reburning with the new lignite sample, and negotiation of a subcontract with the Kansas State University. At higher stoichiometry (SR2>0.9), NO reduction with the new lignite sample is not as effective as the previous sample, but it is comparable with the reburning efficiencies of North Dakota lignite and methane. At the optimal stoichiometry, SR2=0.9, the reburning efficiency is identical to the previous sample.

I. INTRODUCTION

Combustion is the most viable technology using coal's (and lignite's) energy. However, widespread promotion of coal and lignite as the combustion source will require significant reductions of pollutant emissions. One particular class of emission contaminant, nitrogen oxides (NO and NO_2) and nitrous oxide (N_2O), has come to be considered a criterion pollutants due to its contribution to acid rain, stratosphere ozone depletion, troposphere photochemical smog through ozone accumulation, and green house effects.

Development of advanced technologies for the control of these nitrogen containing pollutants at their sources requires knowledge concerning their formation and destruction mechanisms. This knowledge has already been transformed into a number of successful NO_x control technologies, including low NO_x burner, staged combustion, and selective catalytic/noncatalytic reduction.

One of the staging processes, reburning, utilizes in-situ hydrocarbons as NO_x reduction agents in the furnace, which has been demonstrated to be a very attractive NO control technology. In its early development, only natural gas has been considered a potentially effective candidate for reburning fuel. The effectiveness of NO reburning with nature gas has been generally attributed to the strong reducing free radicals derived from natural gas, including C, CH and CH_2. Heterogeneous mechanisms have not been considered a major route of NO reduction during reburning. Nevertheless, our recent studies (Chen *et al.*, 1991; Chen *et al.*, 1992) have indicated that lignite char can be an even more active reburning fuel than methane. This observation is based on simulated reburning tests of two lignites on reactors of two scales. The two lignites tested were selected from Mississippi and North Dakota. Based on the initial screening tests, it has been demonstrated that the lignite char surface participates in heterogeneous/catalytic NO reduction to HCN, while North Dakota lignite ash enhances catalytic HCN reduction to NH_3. Both reactions are important in the overall NO reduction scheme.

A critical review of the recent literature indicates that NO participates in two types of reactions; both are potentially significant to NO reduction in the reburning environment. It has been shown that the carbon in the char may be gasified by NO to form CO, CO_2 and N_2. Recent literature also indicates that calcium sulfide, CaS, serves as a catalyst for reaction $NO + CO \rightarrow CO_2 + \frac{1}{2}N_2$. Since calcium in coal reacts with sulfur, thereby forming CaS during combustion, and the reburning zone is rich in CO, the potential impact of CaS on reburning is a subject yet to be investigated. Both the char gasification and CaS catalyzed reaction discussed above could be enhanced by the highly porous nature of lignite char, which may be the cause of the difference in activities between bituminous char and lignite char.

Our previous observation about the effectiveness of lignite char in the reburning environment is certainly qualitatively consistent with that of the char gasification study in an isolated environment. The relative significance of catalytic effects of minerals, e.g., CaS, in reburning is uncertain.

The objective of this research is to conduct further screening on the NO reduction mechanisms during reburning. The emphases will be placed on rate measurements of the rates of lignite char gasification by NO and the ash catalyzed NO and CO reaction.

II. Scientific Background

A. Heterogeneous Nitric Oxide Reduction Mechanisms

The concept of reburning was first introduced by Wendt *et al.* (1973). It involves a secondary fuel supply (less than 20% of total) and a secondary air injection to produce a fuel rich second stage and a fuel lean third stage, respectively. Tests on a full-scale boiler at Mitsubishi Heavy Industries (Takahashi *et al.*, 1983) resulted in over 50% NO_x reduction. The attractive results led to subsequent efforts at Acurex Corporation (Mulholland and Lanier, 1984), at Energy and Environmental Research Corporation (Greene, *et al.*, 1984; Overmore, *et al.*, 1986) and at the U.S. Environmental Protection Agency (Mulholland and Hall, 1986). A number of operational variables have been identified, including the nature of the reburning fuel (Burch *et al.*, 1991a). Since reburning has demonstrated its high NO reduction and its ability to retrofit conventional coal fired boiler, a systematic engineering analysis appears highly desirable.

Effective utilization of reburning relies on knowledge of not only NO reduction mechanisms in the gas phase, but also heterogeneous fuel nitrogen reaction mechanisms. It is known that NO can be reduced through heterogeneous mechanisms. In addition, char nitrogen reactions have a profound influence on NO emissions in the burnout stage of the reburning process.

The literature contains various mechanisms for char gasification by NO. These include Furusawa *et al.* (1980, 1982, 1985), Chan *et al.* (1983), Teng *et al.* (1992), and Levy *et al.* (1981). Furusawa *et al.* (1980) in his work on NO reduction over char (produced by carbonization of the noncaking Taiheiyo coal) has reported that there is a change in the mechanism at 680°C. They suggested the global NO reduction at high temperatures (>680°C) as

$$C + NO \rightarrow CO + \tfrac{1}{2}N_2 \qquad (1)$$

From reaction rate measurements, Chan *et al.* (1983) proposed the following reaction model;

$C + NO \rightarrow C(O) + \frac{1}{2}N_2$ (2)
$CO + C(O) \rightarrow CO_2 + C$ (3)
$C(O) \rightarrow CO$ (4)

where C represents a surface carbon, and the atoms inside the bracket represents adsorbed atoms. There is a general agreement that the first step (chemisorption of NO) is temperature independent. It probably involves addition of NO in an "N-down" configuration, followed by release of N_2 and formation of carbon oxide surface complexes. Reactions (3) and (4) represent the desorption steps of the surface oxides.

Teng *et al.* (1992) has suggested the following reaction mechanisms.

$2C + NO \rightarrow C(O) + C(N)$ (5)
$C + C(O) + NO \rightarrow C(O_2) + C(N)$ (6)
$2C + 2NO \rightleftharpoons 2C(NO)$ (7)
$C^* + C(O)\ NO \rightarrow CO_2 + C(N) + xC^*$ (8)
$C^* + NO \rightarrow CO + C(N) + yC^*$ (9)
$C(O) \rightarrow CO + aC^*$ (10)
$C(O_2) \rightarrow CO_2 + bC^*$ (11)
$2C(N) \rightarrow N_2 + dC^*$ (12)

Reaction (7) is only important at low temperatures (<200°C). Reactions (5) and (6) are dissociative chemisorption on non-rapid turnover sites. The reactions involving C* are the rapid turnover site reactions that yield CO and CO_2. Reactions (10), (11) and (12) reflect formation of surface sites. In summary, Teng *et al.* (1991) have reported that carbon gasification by NO involves the desorption of surface complexes by a process such as reaction (4), i.e.,

$$[\text{Surface Complex}] \rightarrow CO, CO_2, N_2 \qquad (13)$$

The product release process also involves the direct participation of NO in an apparently single step adsorption process:

$$C + NO \rightarrow CO, CO_2, N_2 \qquad (14)$$

The two separate processes, reactions (13) and (14), are hypothesized to be linked through the existence of free sites, (which are created because of the faster desorption of products than product formation) that can rapidly turn over. Unstable surface complexes form at low temperatures due to the NO attack on rapid turnover sites, and majority of the products is found to be CO_2. Above 650°C, NO attacks char on active unoccupied sites. This results in the immediate desorption of gaseous products, such as N_2, CO, and CO_2. This process is reported to be controlled by dissociative chemisorption of NO on carbon surface. They suggested that the change in mechanism (activation energy) observed at 650°C could be partially due to transition from slow desorption of surface complex to release of the products from high turnover sites. They have also indicated that the number of sites was affected by the gasification temperature, although the surface is not altered by temperature.

Levy *et al.* (1981) in their work on NO/char reactions under pulverized coal flame conditions have suggested the reduction of NO by carbon is probably through dissociation of NO on the surface with a rapid surface diffusion of the dissociated atoms to form N_2. The oxygen produced by the dissociation is strongly chemisorbed and will inhibit further reaction, i.e.,

$$NO + 2C \rightarrow C(N) + C(O) \qquad (15)$$
$$C(N) + C(N) \rightarrow N_2 + 2C, \qquad (16)$$

where C represents a surface carbon, C(N) and C(O) represents adsorbed nitrogen and oxygen atoms. The chemisorbed oxygen can either desorb to produce CO or react with CO to form CO_2, i.e.,

$$C(O) \rightarrow CO \qquad (17)$$
$$C(O) + CO \rightarrow CO_2 + C \qquad (18)$$

The char gasification mechanisms discussed above indicate that CO enhances NO reduction by removing the occupied surface oxides, i.e., reaction (3) above (Furusawa *et al.*.

1982; Chan *et al.*, 1983). Combination of reactions (2) and (3) can also be viewed as a char catalyzed reaction

$$NO + CO \rightarrow CO_2 + \frac{1}{2}N_2 \qquad (19)$$

In the study of char gasification without CO in the feed, Furusawa *et al.* (1980) reported 98% conversion of carbon in char to CO during NO gasification at a temperature of approximately 910°C; at higher temperatures, CO formation became even higher. In a subsequent study, Furusawa *et al.* (1982) reported that under fluidized bed combustion temperatures, the addition of carbon monoxide reduced the consumption of carbon in char approximately to zero and the char provided catalytic surfaces for nitric oxide reduction by carbon monoxide as reaction (19) above. However, the effect of carbon monoxide on the NO reduction rate was reduced over the higher temperature range employed for fluidized combustion of coal. It is not yet known if this observation can be extended to pulverized coal temperatures. In a presentation and its subsequent discussion (Levy *et al.*, 1981), it was suggested that CO enhanced gasification depends on reactor wall material, H_2O, O_2, SO_2, and temperature. Discrepancies about the effects of these gases also exist among the groups who participated in the discussion. One of the objectives of this study is to investigate the rate of char gasification without the presence of CO and the rate of char catalyzed CO+NO reaction separately.

As discussed above, char can serve either as a reactant or a catalyst, depending on the operating conditions. Its role may also be affected by its origin, i.e., coal's geological rank and compositions. In a program funded by U.S. Department of Energy, Chen *et al.* (1991) found that the char derived from a North Dakota lignite had an NO conversion (to HCN) efficiency even higher than that of methane and a bituminous coal, and the ash derived from the same lignite had very high HCN conversion (to NH_3) efficiency. This unique characteristic of North Dakota lignite was further proven on a larger scale downfired furnace (Chen *et al.*, 1991). They speculated that there may be a correlation between the high NO reduction efficiency of lignite char and the high NH_3 yield during lignite pyrolysis reported by Freihaut and Seery (1985). Freihaut and Seery reported nitrogen distributions during lignite and coal pyrolysis with a flash-heated electric grid. Since very fine coal particles (-270+325 mesh) were employed under very low ambient pressure (0.001 torr), it was assumed that the mass transfer limitations of volatile transport in the char particles and secondary reactions are minimal. Their data have indicated that nitrogen distribution varies significantly with the coal rank. For the wide range of coal studied, HCN, not NH_3, was the primary pyrolysis product and only a very small portion of the coal nitrogen was converted to NH_3. Bose *et al.* (1988) demonstrated further that, under very short reaction times (< 1 sec) and 1 atm fuel-rich oxidative environment (SR=0.6~0.8), NH_3 is derived from HCN and HCN from tar nitrogen. Their conclusion has been drawn for coals of various rank, including lignite. The ratio of NH_3 to HCN for lignite increases with increasing reaction time and decreasing rank, which are consistent with the speculation of catalytic conversion of HCN to NH_3. Interestingly, the North Dakota lignite used by Chen *et al.* (1991) has a very high (1.69% of dried lignite) content of calcium. In a recent study of reburning (Chen *et al.*, 1992), a Mississippi lignite was found the most effective reburning fuel. This lignite has 3.60% (dried lignite) content of calcium. Nevertheless, the HCN yields from the Mississippi lignite were very high.

In the investigation of catalytic mechanisms in reburning, calcium oxide was added during reburning with methane at SR2= 0.9 (Chen *et al.*, 1992). Addition of CaO does not appear to reduce NO or HCN. Recently, Hansen *et al.* (1992) found that CaO can reduce NO in the presence of CO, i.e., reaction (19) above. However, the presence of CO_2 in the flue gas deactivates CaO by poisoning the active sites. Since the reburning zone gas always contains CO_2 carried from the primary combustion zone, CaO does not appear to be a practical catalyst for NO reduction in reburning. Interestingly, this observation is consistent with the observation of low NO production in reburning reported by Chen *et al.* (1992).

Hansen *et al.* (1992) also reported significant NO reduction using CaS even in presence of CO_2 in the circulating fluidized bed combustion conditions. Huffman *et al.* (1990) in their work on the behavior of basic elements during coal combustion reported that calcium is dispersed in coal macerals and is bonded to the oxygen anions. During combustion, this calcium present in lignite agglomerates and eventually forms CaO and CaS. Hoping the catalytic activity would be demonstrated at pulverized reburning conditions, CaS was added during reburning with methane (Chen *et al.*, 1992). Contrary to our expectations, addition of CaS powder (35 to 50 μm) resulted in only about 10% NO reduction. This observation was made based on a single experiment, and the differences between the two observations might be caused by the differences the temperature, CO concentration, residence time, and CaS/gas contact area among these studies. The exact cause is not yet known, but the temperature effect (fluidized bed vs. pulverized) on the catalytic activity of CaS to reaction (19) will be a important factor for future investigation. As discussed earlier, Furusawa *et al.* (1982) observed high char-catalyzed NO+CO reaction rates under fluidized bed temperatures, while Levy *et al.* (1981) observed high char gasification rates under high temperature pulverized-coal combustion conditions. It possible that char/CaS catalyzed CO+NO reaction plays a minor role in NO reduction during reburning.

B. Program Approach

The proposed three-year program is aimed at better understanding of the NO reburning mechanisms involving char derived from lignites and bituminous coals. Specifically, we will perform the following

1. Establish baseline reaction rate by collecting data in reburning environment around stoichiometric ratio (SR2) = 0.90 and temperature in the range 800 to 1150°C. NO reburning by one bituminous coal and two lignites will be examined. The NO/char reaction rates will be expressed by internal surface areas based on the fractal dimension concept.

2. Determine the gasification rate of chars (derived from two lignite and one bituminous coal) in the presence of NO, and the effects of CO and CO_2 concentrations on the char gasification rate. Again, the rate of the NO/char reaction will be based on internal surface areas derived from the fractal concept.

3. Determine the reaction rates of CO and NO with and without ash; and from the rate measurements, also determine if char gasification or catalytic CO+NO reaction dominates NO reduction under pulverized coal combustion conditions. Ash catalyzed CO+NO reaction rates will also be expressed by internal surface areas based on the fractal concept.

III. TECHNICAL PROGRESS

A. Reassembly of the Flow Reactor System

The experiments reported here were carried out in a ceramic flow reactor (Figure 1) with a simulated flue gas consisting of 16.8% CO_2, 1.95% O_2, and 0.1% NO in a helium base. These concentrations of CO_2, 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.

The flow reactor used for this research was an alumina tube (Coors Ceramics Co.) with an inside diameter of 1.91 cm and an overall length of 64 cm. The central portion of the reactor tube was enclosed in a 30-cm long, electrically heated furnace (Lindberg Model 55035), which provided tube temperatures up to 1150°C.

Furnace temperature profiles were determined by both centerline traverse and wall mounted type K thermocouples. These two methods agreed within ±5°C. The furnace produced a parabolic axial temperature profile with a relatively flat peak (±20°C) over approximately 20 cm of the heated length. Outside the zone of maximal heating, the temperature fell rapidly at a rate of approximately 60°C/cm. For typical flow conditions, this corresponds to heating and cooling rates on the order of 2000°C/s. Furnace temperature profiles with and without combustion produced identical temperature profiles except for a narrow zone of maximum heat release where both wall mounted and centerline thermocouples exhibited an approximate 10°C rise.

The centerline temperature measurements were taken using a 0.32 cm o.d. sheathed but unshielded thermocouple. Due to high radiation from the walls, the temperature profiles obtained by this method are more representative of the wall temperature than the mean gas temperature at any given location. Using property data for the simulated flue gas composition and the method of Sellars *et al.* (1956) the maximum gas temperature is estimated to be 50°C lower than the maximum wall temperature and to be maintained for only 10 cm of the furnace length. The estimated average gas temperature and reaction time for this 10-cm zone are the basis for the data analysis presented here.

This assignment of an accurate reaction temperature is complicated by the variety of fuels used. Variations in the required induction time may cause the bulk of the reaction to take place before the maximum gas temperature is reached. Since many of the radical species important in reburning are short-lived, the most appropriate reaction temperature may be somewhat lower than that reported.

All of the gas flows were measured individually with specifically calibrated rotameters, as shown in Figure 1. The gas mixtures, with certified composition, were purchased from Matheson Gas Products Inc., Liquid Air Corp., or Liquid Carbonic.

For experiments with coal as the 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.*, 1991b). Part of the gas flow (usually helium) was diverted through the coal feeder as a carrier gas.

The sampling train consisted of 0.635 cm, stainless steel transfer lines and a switching manifold with stainless steel valves. Transfer lines from the reactor tube exit to the impinger were heat traced (80°C) to minimize adsorption of HCN and NH_3. The effluent was desiccated with anhydrous calcium sulfate before transfer to the instrument package through 0.635 cm 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 onto 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 NH_3 in the filter. A 10 μm 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.

Fixed gas species of interest were monitored by an on-line instrument package. The analysis included NO_x (chemiluminescence, thermoelectron), O_2 (paramagnetic, Beckman),

CO and CO_2 (infrared, Beckman). Differences between the base gas used for the calibration gas and sample gas were found to produce significant instrument error. This is particularly true for chemiluminescent NO_x measurement, which relies on a constant gas flow through capillary tubes. Thus each of these instruments was calibrated with a gas mixture representative of the feed gas composition.

HCN and NH_3 were collected by diverting the reactor effluent through a straight tube impinger filled with 0.5 L of 0.1N HNO_3 aqueous solution for a specified time interval. The captured solutions were pH adjusted with NaOH and analyzed for CN^- and dissolved ammonia with specific ion electrodes (Orion Research). Poisoning of the cyanide electrode by sulfur ions was prevented by adding an aqueous solution of $Pb(NO_3)_2$ 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 22% for HCN (in the range of 100 to 700 ppm of HCN). Thus, NH_3 values have been presented as measured while HCN values reported have been corrected for collection efficiency.

To insure the integrity of the data, replicate experiments were run at most conditions. Also, the reactor tube was cleaned frequently to minimize wall buildup of soot or ash. For coal reburning, the tube was cleaned after each run. To eliminate any transient phenomena due to adsorption/desorption, operating conditions were stabilized for at least fifteen minutes before data collection began.

B. Fabrication of a Char/Ash Collection Unit

A char/ash collections device has been added to facilitate solid collection. The is required for 1) the char surface area measurement so that NO+char reaction rate can be better defined, and 2) ash collections in the subsequent experiments of ash-catalyzed

CO+NO reaction.

This solid collection unit includes the previously used solid dumper (a 300 cc stainless steel cylinder) and a filter cartridge which allows expedited solid collections between runs, as shown in Figure 4 and 5. During the experiment, the char or ash is collected on a 0.3 μ filter paper by gravity and the flue gas flows through a side tube on the stainless steel cylinder, not through the filter (which is caped at the other end). The filter holder (Fisher Scientific 09-753-13C) is the same type of unit specified by the EPA for the fly ash collection which has been described in Modified Method 5 (Schlickenrieder, *et al.*, 1985). To avoid water condensation, the stainless steel cylinder and the filter holder were maintained at 110°C by a heating tape during the reburning experiments. The solid sample on the filter were removed between runs with minimum interruption.

C. Sample Preparation

To ensure enough supplies of representative samples for the next three years, an new Mississippi lignite sample (about 30 lb) was collected in a field about 15 miles southwest from Batesville, Mississippi. This was the same site where the last lignite sample (used in our 1992 reburning experiments) was collected. The lignite sample was mechanically ground, sieved, and stored in glass vials which are sealed with tapes to minimize contact with air. Since the optimal particle size range for the coal feeder requires the use of 60 to 140 mesh particles (Chen *et al.*, 1991), possible variations in elemental compositions among the three different sizes (whole sample, 60 to 200 mesh, and <200 mesh) were checked by Huffman Laboratory. No notable differences were observed and the results for a sample of 60 to 200 mesh particles are shown in Table 1 along with the two other samples which will be used in the subsequent reburning experiments: a Pittsburgh No. 8 bituminous coal and a North Dakota lignite.

D. Reburning with the New Lignite Sample

Three reburning experiments have been performed with the new Mississippi lignite after the reactor system was reassembled. The reburning conditions of this experiment were in the same operation range of our previous experiments (Chen *et al.*, 1991; Chen *et al.*, 1992) to check the system performance, sample peculiarity, and data reproducibility. Figures 5 to 8 present the comparisons of NO, HCN, NH_3 and TFN (total fixed nitrogen; i.e., sum of NO, HCN and NH_3) yields with the past results. At higher stoichiometry ($SR2 > 0.9$), NO reduction with the new lignite sample is not as effective as the previous sample, but it is comparable with the reburning efficiencies of North Dakota lignite and methane. At the optimal stoichiometry, $SR2 = 0.9$, the reburning efficiency is identical to the previous sample.

E. Surface Area Measurement and Subcontract Negotiation

The rate of the NO/char reaction depends on the internal surface area of the char. This area is commonly determined by gas adsorption and the Brunauer-Emmett-Teller (BET) equation (Mahajan and Walker, 1978). One difficulty involved in the interpretation of BET data is its dependence on the pore size distribution of the char, or the cross-sectional area of gas molecules. Smaller gas molecules tend to penetration deeper into the smaller pores and results in higher surface area in the measurements. This problem has created difficulty in the estimation of the rate of the NO/char reaction in terms of internal surface area (Levy *et al.*, 1981). Interestingly, with the introduction of fractal concept, surface areas measured based on different gases can be related to one physical property of the char, fractal dimension, and the rate of the heterogeneous reaction can be independent of the size of gas molecule used in the BET measurement (see, e.g., Mandelbrot, 1977; Fan *et al.*, 1991). On December 21, 1993, the University of Mississippi and the Kansas State University has completed the negotiation of a subcontract on the measurements of char and ash surface areas, and on the interpretation of the heterogeneous reactions rates with fractal concepts.

F. Related Technical Activities

The principal investigator co-chaired an air pollution session and presented a paper entitled "Formation and Destruction of Nitrogen Oxide during Coal Combustion" in the Second Mainland-Taiwan Environmental Protection Seminar held in Taipei, Taiwan, December 21-23, 1993. After the meeting, he visited the Energy and Resources Laboratories of the Industrial Technology Research Institute (ITRI), National Cheng-Kung University, and Tunghai University. Seminars on nitrogen oxide control technologies were delivered, and possible full-scale tests of reburning with lignite at ITRI combustion facility have been discussed. A copy of his presentation at these occasions is attached as Appendix in this report. No DOE funds was incurred during this trip.

IV. WORK FORECAST

In the next quarter, we will focus on the establishments of baseline reaction rates by collecting data in reburning environment around stoichiometric ratio (SR2)=0.90 and temperature in the range 800 to 1150°C. Nitrogen oxide reburning with one bituminous coal and two lignites will be examined. The NO/char reaction rates will be expressed by internal surface areas based on the fractal dimension concept.

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Table 1. Ultimate Analysis of Coals*

Contents (%)	Previous MS lignite	New MS lignite	ND lignite	Pittsburgh #8 bituminous
Moisture	7.14	0.99	14.39	2.02
Carbon	55.57	53.16	60.63	70.48
Hydrogen	5.00	5.19	4.44	4.66
Oxygen, by Difference	22.56	16.11	22.63	8.53
Nitrogen	1.32	0.65	0.86	1.44
Sulfur	0.86	0.86	1.19	3.35
Ash	14.69	24.03	10.25	11.54

* Moisture was determined by loss on drying in air at 105°C for one hour. All other results are reported on a dried sample basis.

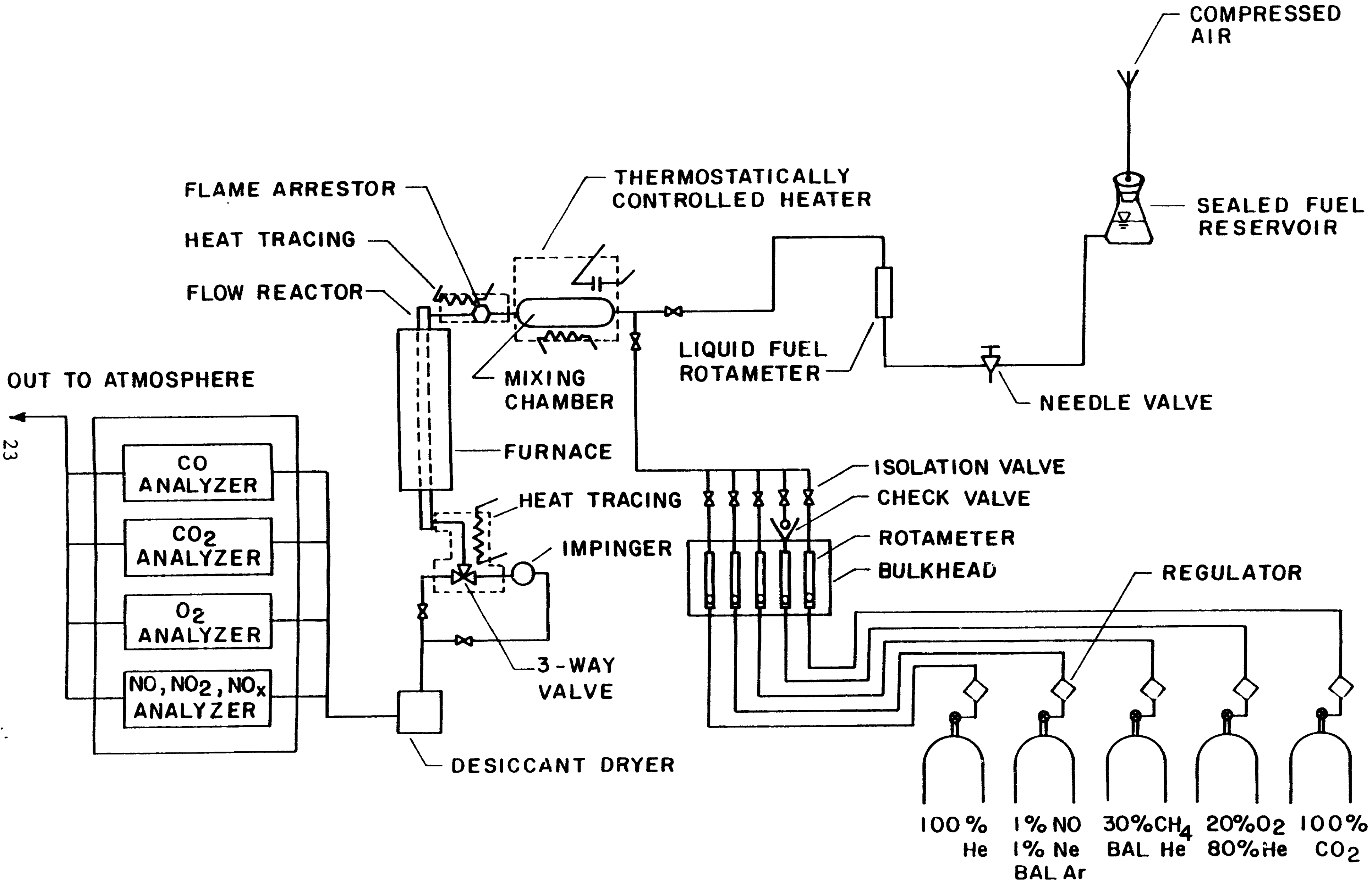


Figure 1. Flow Reactor System

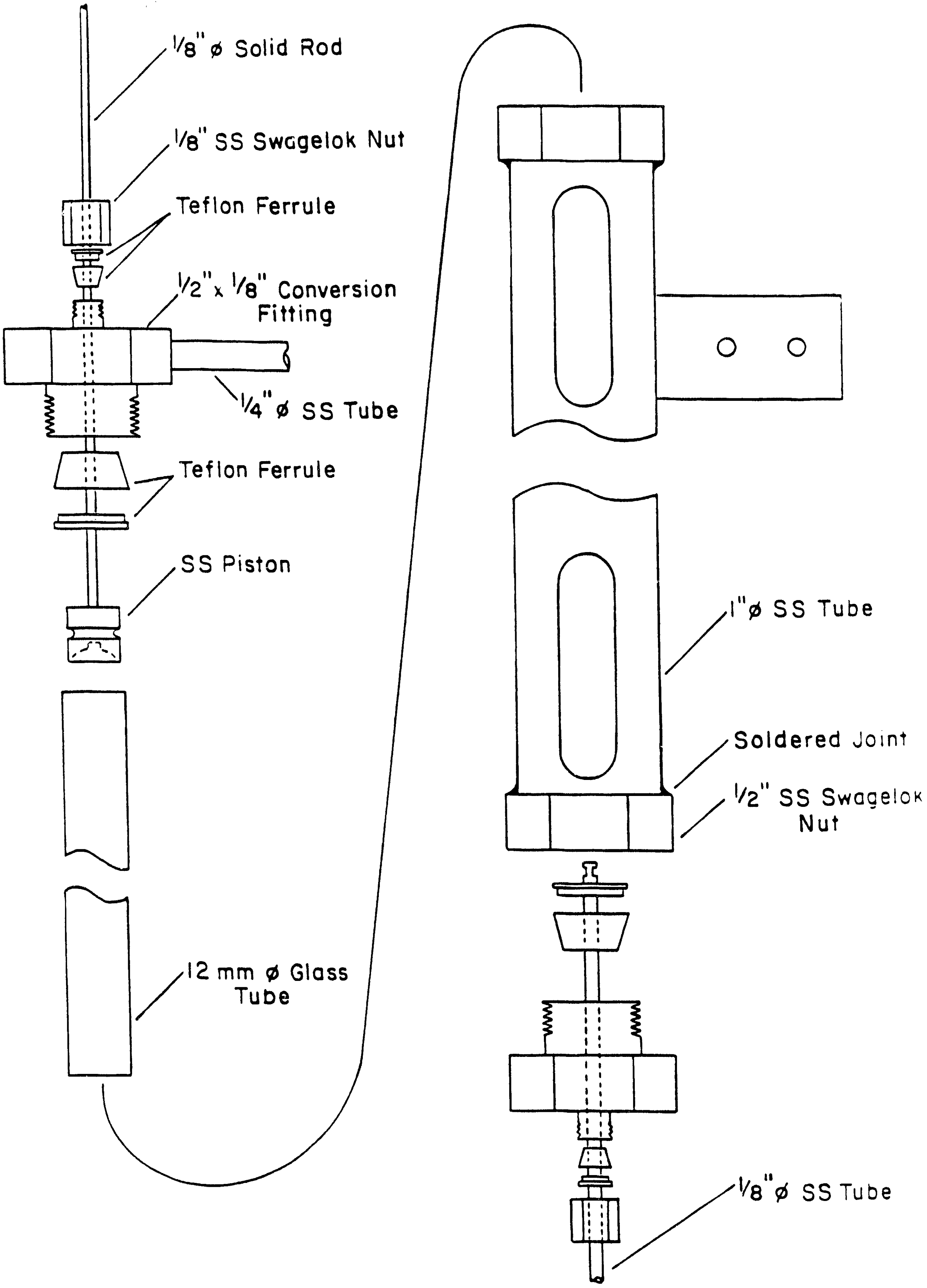


Figure 2. Coal Feeder

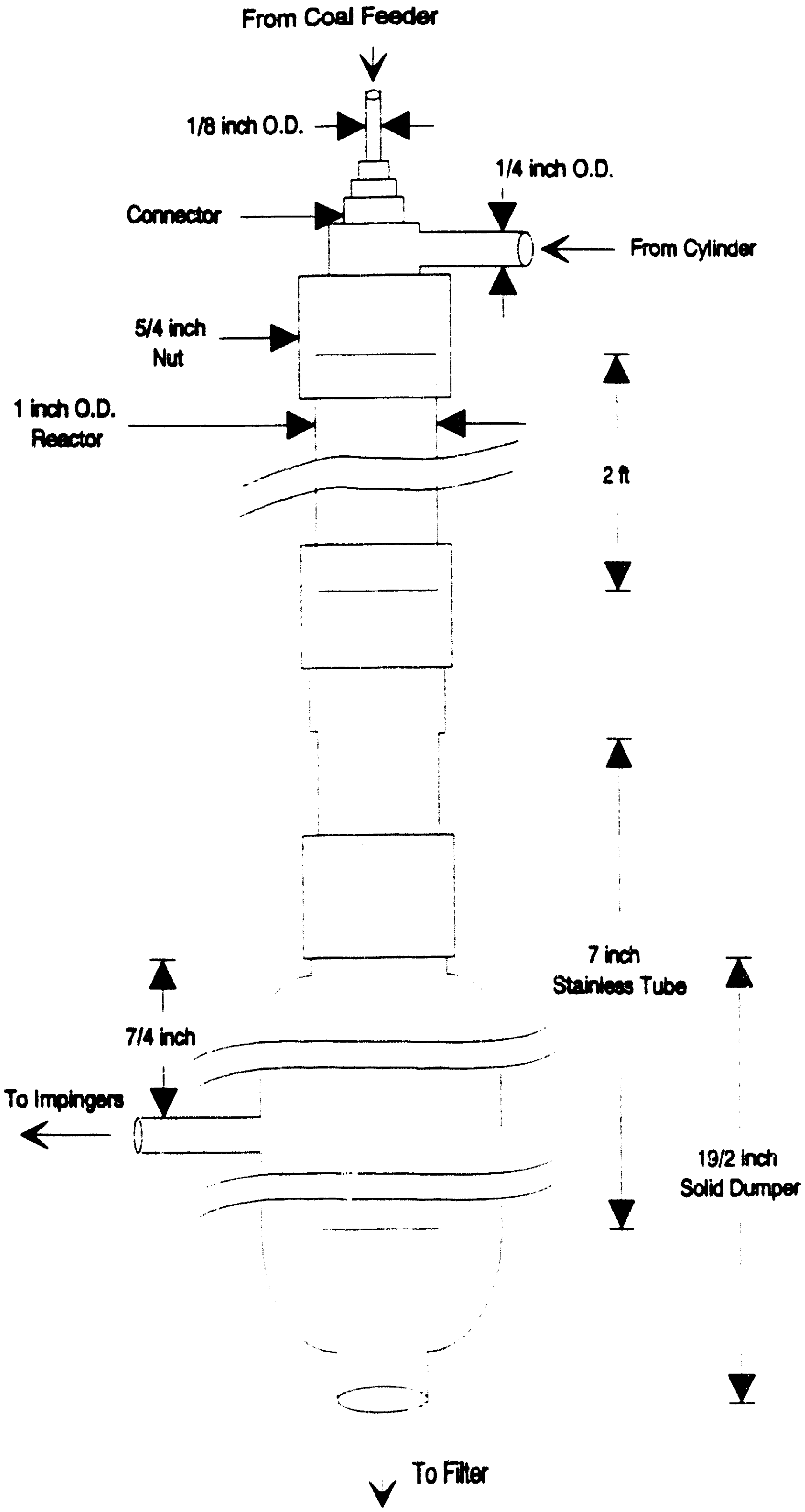


Figure 3. Reactor and Char/Ash Collector

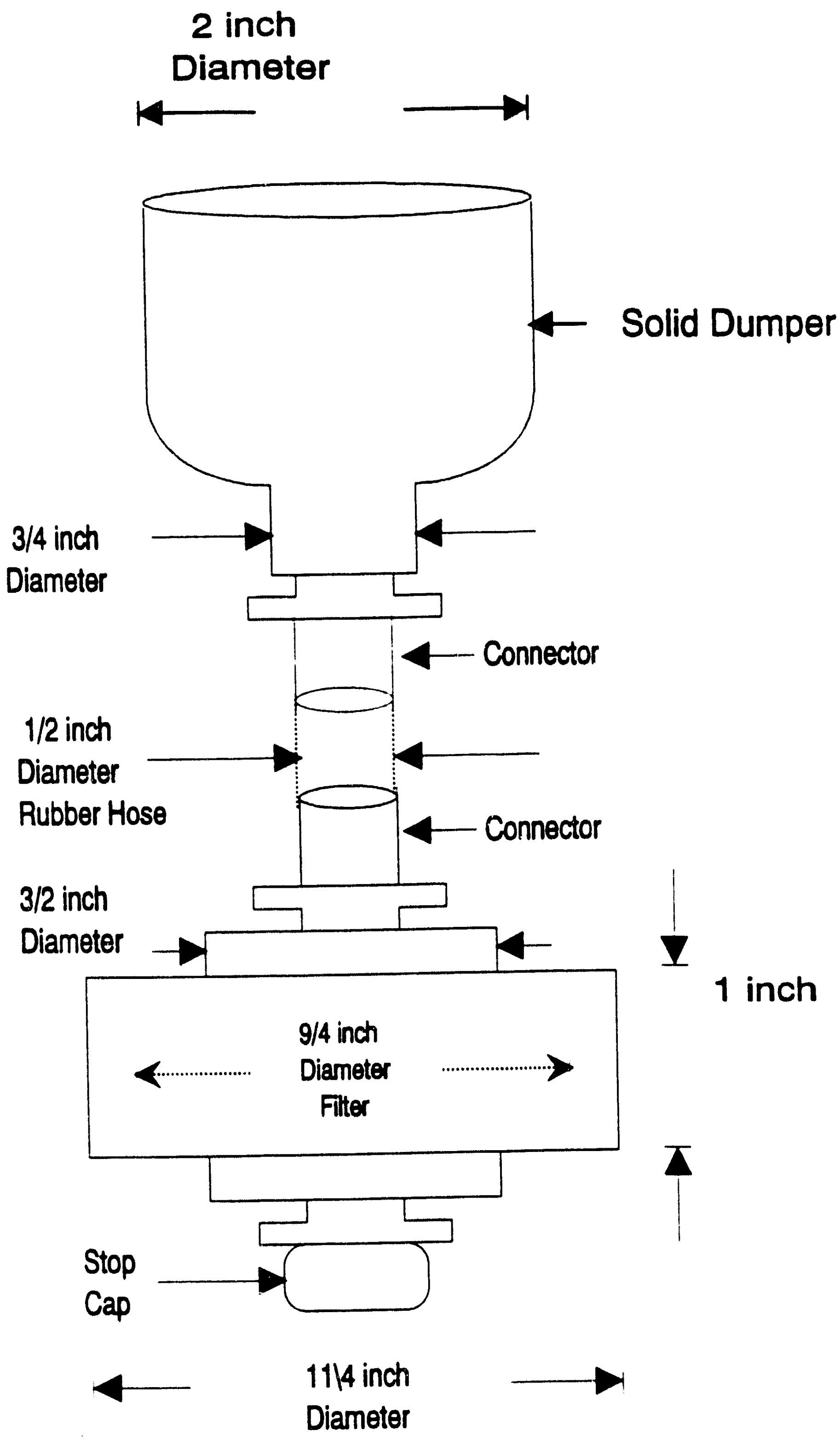


Figure 4. **Filter Part of the Char/Ash Collection Unit**

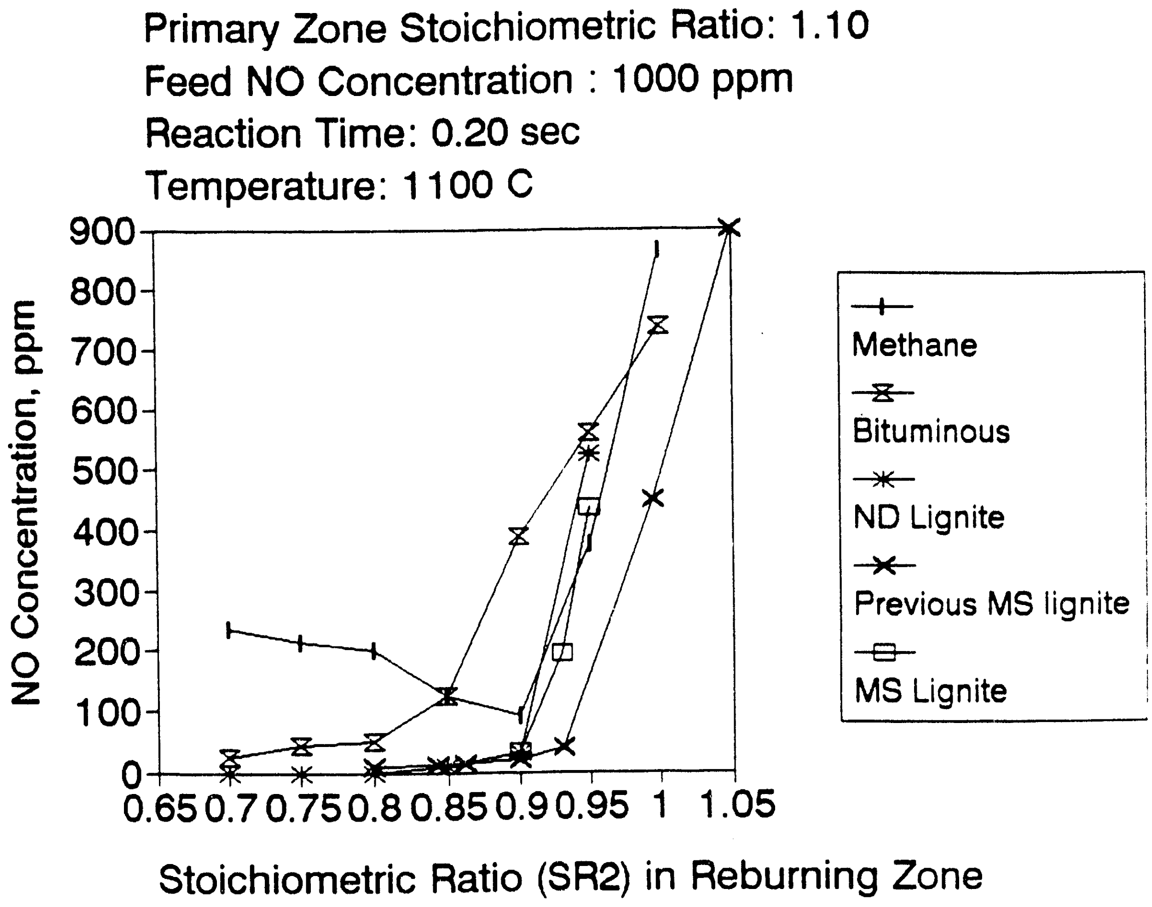
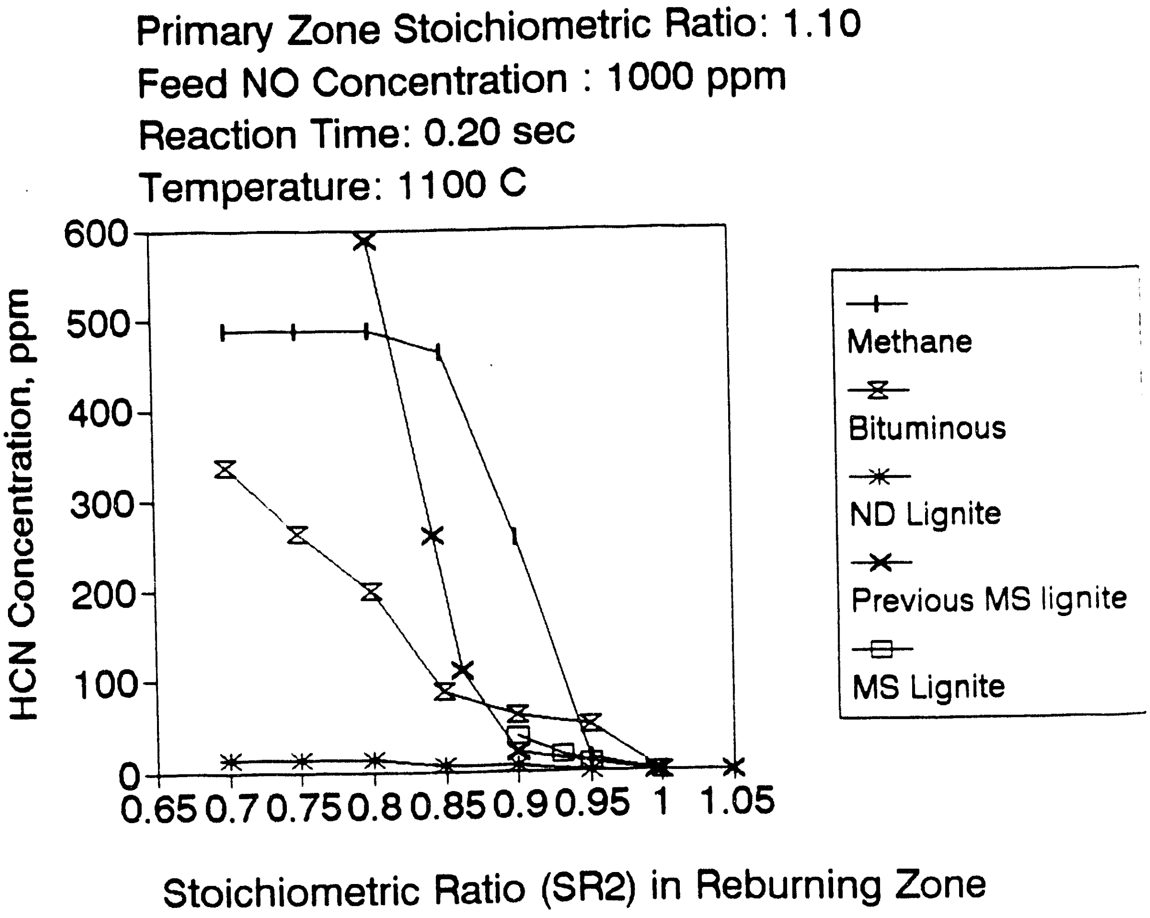


Figure 5. Effects of Reburning Fuels on NO Exit Concentration



Primary Zone Stoichiometric Ratio: 1.10
Feed NO Concentration : 1000 ppm
Reaction Time: 0.20 sec
Temperature: 1100 C

Figure 6. Effects of Reburning Fuels on HCN Concentration

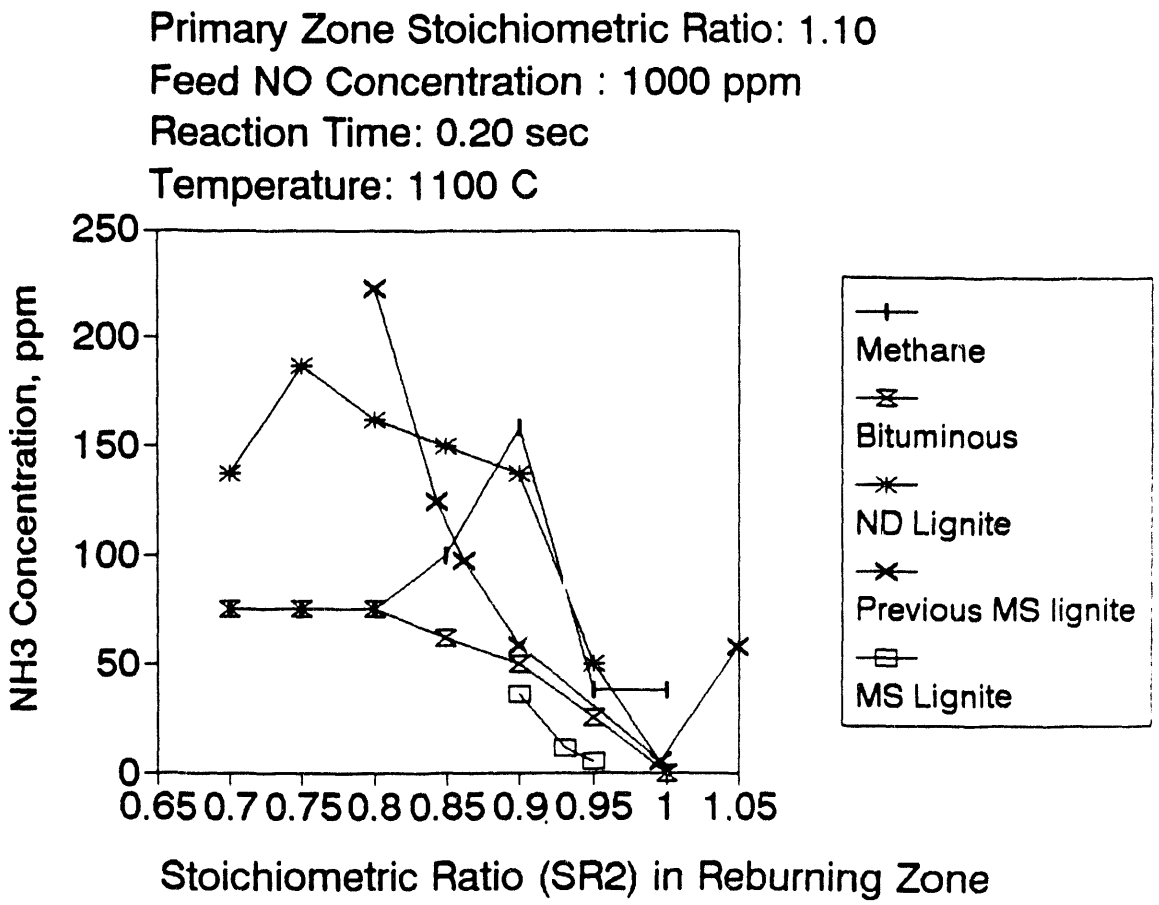


Figure 7. Effects of Reburning Fuels on NH3 Concentration

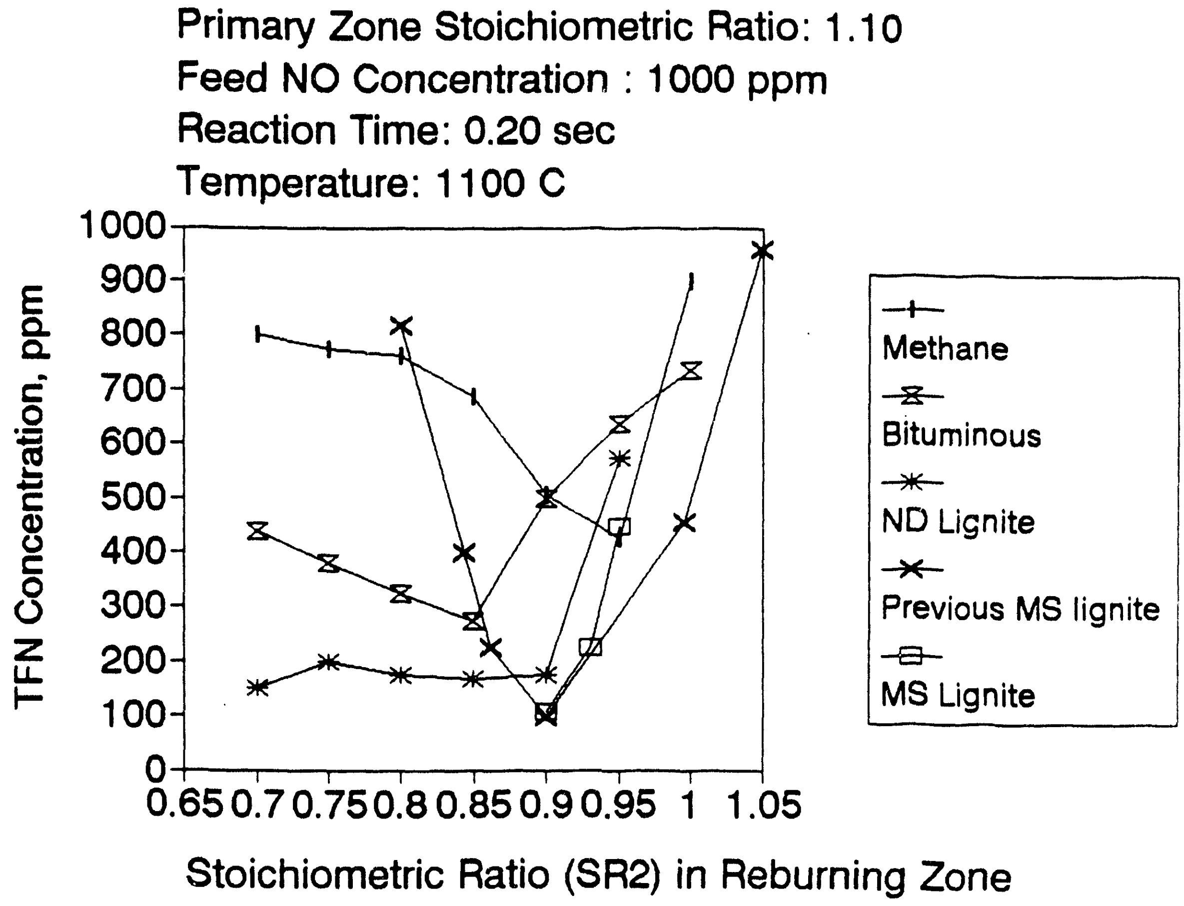


Figure 8. Effects of Reburning Fuels on Yields of Total Fixed Nitrogen (TFN) Species (NO+HCN+NH3)

APPENDIX

FORMATION AND DESTRUCTION OF NITROGEN OXIDES DURING COAL COMBUSTION

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FORMATION AND DESTRUCTION OF NITROGEN OXIDES DURING COAL COMBUSTION

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ABSTRACT

The first segment of this paper addresses the present knowledge concerning the formation and destruction mechanisms of 1) nitrogen oxide (NO) during pulverized coal combustion, and, 2) nitrous oxide (N_2O) during fluidized bed coal combustion. Technologies aimed at control of these pollutants will also be presented. The second segemnt discusses the two on-going projects at the University of Mississippi. The first project concerns the NO reduction through a three stage operation called "reburning," and the second project is directed toward better understanding of N_2O formation kinetics during fluidized bed coal combustion.

INTRODUCTION

Widespread promotion of coal and lignite as the combustion source will require significant reductions of pollutant emissions. One particular class of emission contaminant, including nitrogen oxide (NO) and nitrous oxide (N_2O), has been designated as one of the six criteria pollutants. Although the global emissions of NO and N_2O are decreasing in the last decade, this class of pollutants has been gaining attention important roles in the environment through acidification, forest damage, smog formation, direct and indirect damage to human health, depletion of the stratospheric ozone layer, and the greenhouse effect (Sloss *et al.*, 1992; Boardman and Smoot, 1993; Clement and Kagel, 1990).

Development of advanced technologies for the control of these nitrogen containing pollutants at their sources requires knowledge concerning their formation and destruction mechanisms. This knowledge has already been transformed into a number of successful NO control technologies, including low NO burner, staged combustion, and selective catalytic/noncatalytic reduction.

Concern about the roles of NO in these detrimental effects has also led to the introduction of regulations on its emissions. The U.S. Clean Air Act Amendments (CAAA) of 1990 (see, e.g., Moyer and Francis, 1992) mean significantly more stringent air emissions requirements for the power generation sources. The amendments establish SO_2 and NO_x ($NO+NO_2$) emission reduction requirements and also implement radical changes in treatment of NO_x as a non-attainment pollutant. Title IV, Control Requirement, targets a NO_x reduction of two-million-ton per year. In order to achieve this goal, EPA has been directed to establish the NO_x emission limit at 0.45 lb of $NO_x/10^6$ Btu for tangentially fired boilers and 0.50 lb of $NO_x/10^6$ Btu for wall-fired boilers. The previous emission standard (CAAA of 1977) was set at 0.60 lb of $NO_x/10^6$ Btu for all stationary boilers. In addition to Title IV, Title I of the CAAA of 1990 demands that the states with ozone non-attainment areas classified as serious, severe, or extreme will require volatile organic compounds and NO_x Reasonably Available Control Technology (RACT) limits applied to stationary sources with the potential to emit 50, 25, or 10 tons per year, respectively. Although N_2O emission is not regulated at this time, N_2O has been gaining increasing attention in the last decade due to its detrimental role in the greenhouse effect and ozone depletion in the stratosphere (Mann *et al.*, 1992; Tirpak, 1987; Hao, 1986), its increasing trend (~0.3% per year) and its stable nature.

NO REACTIONS AND CONTROL TECHNOLOGIES

Stationary combustion accounts for more than 52 percent of the total emissions. It is generally believed that NO can be formed by two chemical mechanisms: thermal fixation of atmospheric nitrogen (thermal NO) and the oxidation of nitrogen-containing fuel (fuel NO). Interestingly, mobile combustion systems are the major source of thermal NO, and stationary combustion sources account for most of the fuel NO. Nitrogen oxide is the primary NO_x component produced in combustion processes, and it is oxidized to NO_2 in the atmosphere and becomes a major precursor of acid deposition.

A mechanism for the thermal NO formation was first postulated by Zeldovich (1946) and was later extended to fuel-rich combustion ("Extended Zeldovich Mechanism") by considering the presence of OH (reaction 3 below; Fenimore, 1971):

$$O + N_2 \rightleftharpoons NO + N \quad (1)$$

$$N + O_2 \rightleftharpoons NO + O \quad (2)$$

$$N + OH \rightleftharpoons NO + H \quad (3)$$

The large activation energy of the rate controlling reaction (1) suggested a strong dependence of NO yield on temperature. The extended Zeldovich mechanism adequately described NO formation in the post-flame region, but failed to explain the "prompt NO" formed rapidly in the flame front. The lack of O atoms in the flame front limits the formation of NO via the extended Zeldovich mechanism. Fenimore's study further led to the discoveries of the interaction between hydrocarbon free radicals and nitrogen molecules; such as:

$$CH + N_2 \rightarrow HCN + N$$

A portion of the HCN is subsequently oxidized to NO.

Most nitrogen in coal is believed to be chemically bound in the aromatic ring structure. During high temperature pyrolysis, HCN and NH_3 are the two major nitrogen-containing compounds. In combustion, HCN is subsequently converted to amines NH_i. The amines are then either oxidized to NO or converted to N_2 by reactions with nitric oxide or other amine species. The global reaction can be described as

$$\text{coal} \rightarrow \ldots \rightarrow HCN \rightarrow NH_i \begin{array}{l} \xrightarrow{OH,\ O} NO \\ \xrightarrow[NH_i,\ NO]{} N_2 \end{array}$$

Destruction of NO can be achieved through a number of chemical reactions The most commonly used chemicals in large-scale plants are hydrocarbons, ammonia or urea. Other chemicals which have been tested in research work include amines, amides and amine salts and cyanuric acid. The use of hydrocarbon fuel for the reduction of NO is the basic concept behind the design of low NO_x burner and multistage combustors. Methods involve the use of nitrogen-containing additives are called selective non-catalytic reduction (SNCR). The reaction is selective which means that oxidation of added reagents and sulfur dioxide should not occur. When ammonia is used along with a catalyst, it is usually called selective catalytic reduction (SCR).

Fundamental understanding of nitrogen chemistry in combustion experienced major advancements in the last decade due to the developments of two basic tools laser technologies and high speed computing. With the progress in laser diagnostic techniques, many simple stable and transient species at low concentrations can be analyzed (see, e.g., Eckbreth, 1988). From the theoretical point of view, gas phase nitrogen reaction mechanisms were examined in detail by Miller and Bowman (1989). They used the CHEMKIN-II kinetic analysis package (Kee *et al.*, 1989) along with a mechanism which contained 234 possible elemental reaction steps in their review of NO formation and destruction in C1 and C2 hydrocarbon gases. From the sensitivity analysis code of CHEMKIN (Lutz *et al.*, 1987), it is shown that the majority of NO is reduced by radicals C, CH and CH_2 to HCN and amine radicals (NH_i). The amine radicals, in turn, can be converted to N_2 or NO. The key reactions include

$$C + NO \rightleftharpoons CN + O$$
$$CH + NO \rightleftharpoons HCN + O$$
$$CH_2 + NO \rightleftharpoons HCNO + H$$

The reducing capacity of hydrocarbon fuels has generated two approaches to NO control: low NO_x burner and staged combustion. They are viable candidates for retrofitting the conventional combustors. Low NO burners are designed to achieve delayed combustion through the way in which air and fuel are introduced. By staging the additional air, coal devolatilization takes place under low stoichiometry, promoting the conversion of fuel nitrogen to N_2, not NO. Reburning, or fuel staging, is aimed to reduce the NO formed in the primary combustion zone to N_2 by introducing a secondary fuel which accounts for about 10 to 20% of total energy output. Both natural gas and coals have been tested as the secondary fuel.

From similar optical-based diagnostic measurements and detailed kinetic analysis, the important reaction steps during SNCR have been elucidated:

$$NH_2 + NO \rightleftharpoons NNH + OH$$
$$NH_2 + NO \rightleftharpoons N_2 + H + OH$$
$$NH_2 + NO \rightleftharpoons N_2 + H_2O$$

SNCR is usually conducted under 900-1100C.

During SCR, ammonia is first absorbed on catalyst followed by NO/NH_3 surface reactions (to N_2 and H_2O) and catalyst regeneration by oxygen (Schumacher, 1988). Titanium oxide based catalysts now completely dominate the market, although zeolite and iron oxide based catalysts have also been employed. It is usually conducted under 270-430C.

NO control technologies and reactions mechanisms have recently been reviewed by Sloss *et al.*, (1992) Bowman (1991), and Boardman and Smoot (1993). Current demonstration projects sponsored by the U.S. Department of Energy (DOE) can be found in a DOE's report (DOE, 1993).

N_2O REACTIONS

Much significant research on N_2O reaction mechanisms has been reported in the last five years (see. e.g., Mann *et al.*, 1992) since fluidized bed combustion has been identified as a potential source of N_2O emissions [40-250 ppm, at 6% O_2, Amand and Andersson (1989)]. In the homogeneous gaseous systems, nitrous oxide appears to be formed primarily through the reactions (Perry *et al.*, 1985)

$$HCN + O \rightarrow NCO + H$$
$$NCO + NO \rightarrow N_2O + CO$$

The key stable intermediate in this mechanism is HCN which is formed slowly from char nitrogen during fluidized coal combustion. This has been verified by Kramlich *et al.* (1989) and Ernola and Hupa (1989). Alternatively, nitrous oxide can also be formed through amine radical (Dean *et al.*, 1984; Kramlich *et al.*, 1989)

$$NH + NO \rightarrow N_2O + H$$

The homogeneous destruction of N_2O is generally thought to proceed via the reactions (Kramlich *et al.*, 1989; Kilpinen and Hupa, 1990)

$$N_2O + H \rightarrow N_2 + OH \quad \text{at high temperature}$$
$$N_2O + OH \rightarrow N_2 + HO_2 \quad \text{at low temperature}$$

De Soete (1988, 1990) has shown that heterogeneous formation of nitrous oxide on char may occur through solid-bound CNO and CN groups, i.e.,

$$2(CNO) \rightarrow (CO) + (C) + N_2O$$
$$NO + (CN) \rightarrow N_2O + (C)$$
$$(CNO) + (CN) \rightarrow 2(C) + N_2O$$

where the parentheses denote solid-bound groups. De Soete also proposed heterogeneous N_2O decomposition reactions through carbon and solid-bound CO

$$N_2O + (C) \rightarrow N_2 + (CO)$$
$$N_2O + (CO) \rightarrow N_2 + CO_2$$
$$N_2O + (CO) \rightarrow 2NO + (C)$$

Catalytic reduction of N_2O by metals and metal oxides has also been reported by a number of research groups. Budininkas (1976) reported that, in isolated environment, the most active catalysts for N_2O decomposition were Ru, Pt, and Rh, followed by oxides of Ni and Co. With their objectives aimed at reduction of nitrous oxide during fluidized bed coal combustion, Miettinen *et al.* (1991), and Lisa *et al.* (1991) examined a series of metal oxides in the temperature range 600-1000C. Both groups reported high N_2O decomposition efficiencies over CaO beds. Miettinen *et al.* reported high activities on Fe_3O_4, Fe_2O_3 and MgO. Lisa et al. reported relatively weak activities of sulfated limestone, peat ash, and quartz sand (SiO_2). Addition of O_2 reduced the activities of CaO slightly, and addition of water increased the activities. Lisa et al. also studied N_2O formation from ammonia in different beds, and sizeable amounts of N_2O were observed only from the CaO bed. Hansen *et al.* (1992) have reported that both CaS and CaO are active catalysts during circulating fluidized bed coal combustion.

RESEARCH AT UNIVERSITY OF MISSISSIPPI

Two projects are currently active at the University of Mississippi: 1. Role of Char during Reburning of Nitrogen Oxide; and 2. Nitrous Oxide Formation and Destruction in Fluidized Coal Combustion.

Under the financial support of U.S. Department of Energy and the U.S. Bureau of Mines, we have been investigating various mechanisms for the in-furnace reduction of NO in the last few years. It has been discovered recently that NO can be effectively reduced over lignite char surface in reburning. These conclusions have been drawn from tests on reactors of two different scales and two lignites: one from Mississippi and the other from North Dakota. Reburning is a three-stage combustion process designed for NO reduction. The primary combustion zone produces more than 80% of the total energy output similar to a conventional furnace. A small amount of reburning fuel is introduced into the second stage where the majority of NO is chemically reduced to nitrogen. The unburned fuel is then combusted in the third stage by introducing additional air. Coal and lignite have not been considered to be effective reburning fuels, partially because of the inert nature of bituminous char observed earlier. In addition, their nitrogen content could result in additional nitrogen oxide emissions in the burnout stage. What has not been anticipated is the highly active nature of lignite char surface. First, it has been demonstrated in the literature that lignite char can be gasified by nitrogen oxide; second, the minerals in lignite char can catalyze the CO+NO and gasification reaction; and third, lignite char has a highly porous structure which is desirable for gas/solid reactions. The on-going research is aimed at a better understanding of the chemical and physical mechanisms involved in the reburning with chars. Char gasification rates will be measured with and without the presence of CO. Further, the rate of the char catalyzed CO+NO reaction will also be measured. One bituminous coal and two lignites, one from North Dakota and the other from Mississippi, will be used in these tasks. A unique component of this program is the use of the fractal concept in the estimations of these gas/solid reaction rates. The proposed program is designed to investigate the relative importance of these two reactions (char gasification and ash catalyzed CO+NO reactions) under reburning conditions.

The objective of the N_2O project is to investigate theoretically and experimentally the coal (and char) nitrogen reaction pathway in a fluidized bed combustion environment. A recent mechanistic study has implied that delayed evolution of HCN from coal and char could contribute to high emissions of N_2O under relatively low temperatures and short residence time conditions, such as that used under fluidized bed coal combustion. Through direct measurement, fluidized bed combustion has been identified as a principal source of N_2O emissions. While the fluidized bed N_2O data are qualitatively consistent with the proposed N_2O formation mechanism, time resolved HCN evolution profiles under various conditions are a missing link between these two findings. Specifically, the effects of solid fuel particle size, temperature history, fuel properties, and reacting gas composition have been observed to exert significant effects on the formation and destruction of HCN and N_2O. This project is designed to measure the emission rates of these pollutants in fluidized bed combustion environments and their potential interactions. Time resolved profiles of nitrogen species leading to the formation of N_2O will be the focal point of this research. The model contains three major elements: a non-isothermal single particle combustion in a preheated reactor, a gas phase reaction zone, and a plug flow reactor. These elements are designed to simulate the nitrogen chemistry in a circulating fluidized bed.

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