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FORMATION AND DESTRUCTION OF NITROGEN
OXIDES IN COAL COMBUSTION

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TABLE OF CONTENTS

I. Introduction.....	1
II. Technical Progress.....	1
A. Work Accomplished.....	1
1. Shock Tube.....	1
2. NO Recovery	7
3. Analytical Procedures.....	7
2. Down-Fired Furnace.....	8
B. Work Forecast.....	10
C. References	10

I. Introduction

This program addresses the mechanisms of NO reduction in pulverized coal flames using reburning. Using both thermodynamic and kinetic simulation combined with both pilot and bench scale experimental work, we propose to better define the conditions that lead to the destruction of NO, without the concomitant increase in other nitrogenous pollutants. Specifically, the interactions between NO and hydrocarbon constituents in the fuel, and the fate of fuel nitrogen are the focal points of this research. Isotope doped ^{15}N NO is used for tracing the reaction pathways.

Three different experimental apparatus are being used to acquire data under different ranges of operation conditions. A shock tube and a bench scale flow reactor are used to investigate the interaction between NO and various gas, liquid, and solid fuels. The shock tube operates at high temperatures (1000 to 2500 K) and short reaction times (1 to 2.5 ms), while the flow reactor is designed for the investigation of long reaction times (about 1 sec) and relatively low temperatures (up to 1100 C). Much of the work this quarter was devoted to developing the analytical techniques for the analysis of NO via gas chromatography. Experiments will also be performed with a 30 KW/hour down-fired furnace, which has been constructed at LSU especially for this program. During this quarter, the furnace erection was completed, and safety protocol approved.

II. Technical Progress

A. Work Accomplished

1. Shock Tube

Shock tube experiments involving the reduction of NO on hydrocarbons have previously been considered for pyrolysis conditions only. However, experiments conducted in an oxidizing environment are more desirable since they better simulate conditions found in the reburning process. Also, the addition of oxygen changes the nature of hydrocarbon decompo-

sition and increases the radical pool, which is thought to be primarily responsible for the reduction of NO to diatomic nitrogen (N₂) [1].

In the past, shock tube experiments involving both NO and O₂ were deemed impractical because of the known reaction

which proceeds rapidly at ambient temperatures. The gases cannot be premixed and stored prior to use and the time required for thorough mixing in the shock tube is relatively long. Thus, preserving the desired initial gas composition becomes difficult. Minimizing the conversion of NO to NO₂ requires analysis of the time needed for thorough mixing and the degree of conversion of NO that occurs during this time.

The mixing problem is depicted in Fig. 1. Initially the test section of the shock tube is filled to a predetermined pressure with argon containing low concentrations of NO. Other gases such as neon and hydrocarbons may also be present. Oxygen is then introduced through the end plate of the test section and allowed to diffuse through the argon. Thorough mixing is assumed to be achieved when the concentration of oxygen at the ball valve is within 99.5% of the average oxygen concentration.

The mixing problem is governed by the one-dimensional unsteady diffusion equation

$$\frac{\partial c}{\partial t} = \mathcal{D}_{AB} \frac{\partial^2 c}{\partial x^2}$$

with boundary conditions

$$\frac{\partial c}{\partial x}(0,t) = \frac{\partial c}{\partial x}(L,t) = 0$$

and initial condition

$$c(x,0) = c_0 H(x-x_1)$$

The diffusion coefficient $\mathcal{D}_{AB}$ for low pressure is calculated by [2]

$$\frac{P \mathcal{D}_{AB}}{(P_{CA}P_{CB})^{1/3}(T_{CA}T_{CB})^{5/12}(\frac{1}{M_a} + \frac{1}{M_b})^{1/2}} = a \left(\frac{T}{\sqrt{T_{CA}T_{CB}}} \right)^b$$

in which $\mathcal{D}_{AB} = \{\text{cm}^2\text{sec}^{-1}\}$, $p = \{\text{atm}\}$, and $T = \{\text{K}\}$. For non polar gas pairs such as oxygen in argon, $a = 2.745 \times 10^{-4}$ and $b = 1.823$.

At ambient temperature ($T = 300 \text{ K}$), the calculated values of $\mathcal{D}_{AB}$ at various pressures of interest are shown in Table I. Also shown in Table I are the calculated times required for thorough mixing of the gases.

Table I. Diffusion coefficients and mixing times for different test gas pressures.

$P\{\text{Torr}\}$	$\mathcal{D}_{AB}\{\text{cm}^2/\text{sec}\}$	$t\{\text{sec}\}$
760	0.197	11,400
60	2.495	900
45	3.327	675
30	4.990	450

The most notable feature of this information is that reducing the test gas pressure substantially reduces the time required for thorough mixing. But, how do these times compare to the time required to convert NO via reaction (1)?

The best experimental rate coefficients are reaction (1) appear to be [3]

$$k_f = 1.2 \times 10^9 \exp \left\{ \frac{530}{T} \right\} \frac{\text{cm}^6}{\text{mol}^2 \cdot \text{sec}}, T = 273-650 \text{ K}$$

$$-\frac{1}{2} \frac{d[\text{NO}]}{dt} = k_f [\text{NO}]^2 [\text{O}_2]$$

for the forward reaction and

$$k_r = 2.0 \times 10^{12} \exp \left\{ \frac{-13,500}{T} \right\} \frac{\text{cm}^3}{\text{mol} \cdot \text{sec}}, T = 600-2000 \text{ K}$$

$$-\frac{1}{2} \frac{d[\text{NO}]}{dt} = k_r [\text{NO}_2]^2$$

for the reverse reaction.

From these rate constants evaluated at 300 K, we can calculate the equilibrium constant as

$$K = \frac{k_f}{k_r} = 1.22 \times 10^{17}$$

By assuming the oxygen concentration to be constant we can estimate the equilibrium between NO_2 and NO as

$$\frac{\text{NO}_2}{\text{NO}} = (K [\text{O}_2])^2$$

Also, the half life of NO can be evaluated by

$$t_{1/2} = \frac{1}{2k_f [\text{NO}]_0 [\text{O}_2]}$$

The calculated values for the NO₂/NO equilibrium and the NO half life are given in Table II. These calculations represent a mixture containing 1% by volume NO in argon with varying oxygen mole fractions and at various total pressures.

Table II. Equilibrium NO₂/NO ratios and NO half lives at different conditions

%O ₂	P _{total} =760 Torr		P _{total} =60 Torr		P _{total} =45 Torr		P _{total} =30 Torr	
	NO ₂ /NO	t _{1/2} (s)	NO ₂ /NO	t _{1/2} (s)	NO ₂ /NO	t _{1/2} (s)	NO ₂ /NO	t _{1/2} (s)
1	2.3(5)	358	6.6(4)	5.7(4)	5.7(4)	1.0(5)	4.6(4)	2.3(5)
2	3.3(5)	179	9.3(4)	2.9(4)	8.0(4)	5.1(4)	6.6(4)	1.2(5)
3	4.0(5)	119	1.1(5)	1.9(4)	9.8(4)	3.4(4)	8.0(4)	7.6(4)
4	4.7(5)	89	1.3(5)	1.4(4)	1.1(5)	2.6(4)	9.3(4)	5.7(4)
5	5.2(5)	72	1.5(5)	1.2(4)	1.3(5)	2.0(4)	1.0(5)	4.6(4)

The effect of reduced pressure is a slight shift of equilibrium in favor of NO. However, the greater impact is the reduced rate of conversion of NO as evidenced by the extremely long half-life of NO at low pressure.

The combination of enhanced mixing and reduced reaction rate at low pressure allows the specification of experimental conditions for the shock tube that will substantially preserve the initial gas composition. By using the calculated mixing times at each pressure the percentage of NO preserved during mixing has been calculated for various concentrations of oxygen in the mixture. These results are shown in Table III. The calculated values of $\mathcal{D}_{AB}$ and the required mixing times are also shown for convenience.

Table III. NO preserved [%] after mixing for various oxygen concentrations.

P _{test gas} {Torr}	D _{AB} {cm ² /sec}	Time {sec}	%O ₂ in mixture				
			1	2	3	4	5
760	0.197	11,400	3.1	1.6	1.0	0.8	0.6
60	2.495	900	98.5	97.0	95.5	94.1	92.7
45	3.327	675	99.3	98.7	98.1	97.4	96.8
30	4.990	450	99.8	99.6	99.4	99.2	99.0

By establishing a predetermined maximum loss of sample which can be tolerated, we can determine appropriate experimental conditions from the calculations in Table III. However, it should be pointed out, that these calculations have not yet been verified by experiments and should be used with caution.

Another point of interest is the potentially significant reversion of NO₂ to NO at high temperature. The reaction

$$k = 2.0 \times 10^{12} \exp \left(\frac{-13,500}{T} \right) \frac{\text{cm}^3}{\text{mol-sec}}, \quad T = 600\text{-}2000 \text{ K}$$

dominates at temperatures above 1000 K and at 2500 K, the calculated half-life of NO₂ is 1.1 (-4) sec. This is based on a gas mixture at atmospheric pressure containing an initial NO₂ concentration of 1% by volume. Another reaction that contributes to NO₂ reversion is

$$k = 1.1 \times 10^{16} \exp \left\{ \frac{-33,000}{T} \right\} \frac{\text{cm}^3}{\text{mol-sec}}, \quad T = 1400-2400\text{K}$$

which is of the same order of magnitude as reaction (2) at 2500 K.

2. NO Recovery

Kirsch [4], in a previous work on the heterogeneous reduction of NO on carbon blacks, found a substantial loss of NO in high temperature shocks without the addition of a reducing agent (i.e. simply NO in argon). Further investigation revealed significant concentrations of carbon monoxide and hydrocarbons in the post shock gases. Several explanations were offered for the presence of these gases. The most plausible explanations seemed to be diffusion of pump oil into the shock tube and hiding of hydrocarbons and carbon monoxide in the relatively rough walls of the shock tube. However, no evidence of pump oil could be found and calculations showed that diffusion of gases from the walls into the test gas was far too slow to be of any significance during the short residence time at high temperatures.

In separate experiments, Sutherland [5] , while studying the decomposition of ammonia in shock heated gases, found a significant concentration of background hydrogen atoms in shocks supposedly without a hydrogen source. He was able to resolve the problem by changing from mylar to aluminum diaphragms. Apparently, the mylar diaphragms commonly used in shock tube experiments produce a dust when they rupture which pyrolyzes and gives off various hydrocarbon fragments and radicals. We are currently in the process of converting to aluminum diaphragms, and we expect no further problems with poor NO recovery.

3. Analytical Procedures

As stated in the previous quarterly report, our experience with syringe injection has shown significant contamination of the sample with ambient

air despite concentrated efforts to eliminate it. Air contamination poses two major problems in this research. First, the oxygen causes a loss of NO in the sample by converting NO to NO₂. Secondly, the nitrogen contamination prevents an accurate nitrogen balance in the post shock gases.

In order to alleviate this problem, syringe injection has been dropped in favor of static injection with a sample loop as shown in Figure 2. The sample loop is evacuated to less than 1 micron total pressure with a diffusion pump then filled with the test gas from a sample bottle. When the air activated valve is switched, the injection from the sample loop is made onto the column. Using this technique, the total contamination from air is limited to less than .003% of the sample.

Analysis of the reaction products from shock tube runs containing O₂ are more difficult than for pyrolysis runs. Due to the necessary time lag (approximately 30 minutes) between the experiment and the actual gas analysis, a significant amount of the NO contained in the post shock gas would be converted to NO₂. Thus, an accurate analysis of the post shock gas necessarily includes quantitation of NO₂ as well as NO. Analysis of NO₂ is not routine and requires specialized chromatographic columns. We are currently in the process of selecting new columns to allow analysis of NO₂ along with the other gases of interest.

2. Down-Fired Furnace

During this period, the down-fired furnace facility has been assembled and is now ready for gas or pulverized coal firing. A new stainless steel sampling probe has been assembled, since the original probe from Kansas State University, had been lost. One section of the furnace has required new refractory material. The on-line instrumentation, consisting of CO, CO₂, O₂, and NO/NO₂ detectors is now ready for calibration and sampling. Thermocouples to the furnace have also been replaced. Digital and analog outputs have been acquired for the temperature readings.

In preparation for runs with pulverized coal streams doped with NO, a run protocol has been developed to conserve the very expensive isotopi-

cally labeled NO. Given our budget for expendables for the remainder of the project period, we believe that between 10 and 20 runs with isotopically labeled NO will be practicable. During those runs, normal NO will be used in concentrations of up to 10,000 ppm to establish steady-state conditions for our measurements. The isotopically labeled NO will be metered into the NO stream prior to its introduction into the furnace. We will use up to 10 percent by volume of labeled NO for periods of up to 10 minutes during these experiments.

We stress that to our knowledge, we are the first to attempt such large scale testing with labeled NO. While the potential insights that such testing may provide us into the mechanisms of NO reduction under reburning conditions are significant, the risk of being able to conduct enough meaningful experiments is considerable. To minimize the risk, however, we are planning to conduct these experiments very carefully, and only after small scale testing in the shock tube and the bench scale furnace provides us with confirmation that our experimental conditions appear optimal and are worthy of scale-up verification.

Prior to these runs, we are planning to conduct experiments that will confirm our facility's ability to replicate the results of Wendt's team at the University of Arizona. In these experiments, we will inject NO into the post-flame region of a pulverized coal flame and follow the decay of NO with our on-line detectors, and the build-up and decay of intermediates NH_3 and CHN with specific ion analysis of impinger solutions. Consequently, during this upcoming quarter, we will begin accumulating axial profiles of NO decay in rich natural gas and rich pulverized coal flames in preparation for the isotopically labeled work in the Spring.

We are pleased to note that our research team for this segment of the program is now complete with the arrival of Mr. Franz Tillman, a M.S. student in mechanical engineering. He will provide assistance to Mr. Rodger Conway, a research associate in the department, and Dr. Lester, the principal investigator on this portion of the program.

B. Work Forecast

We will concentrate in the next quarter on initial experiments in the shock tube that will begin to delineate the optimal conditions for our larger experiments. Down-fired furnace experiments will be conducted with gas and NO and possibly with pulverized coal and NO to begin testing our unit's ability to provide results consistent with those in the literature.

C. References

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Figure 1. Test section of the shock tube.

Figure 2. Static injection setup for evacuated sample loop.

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