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### Title

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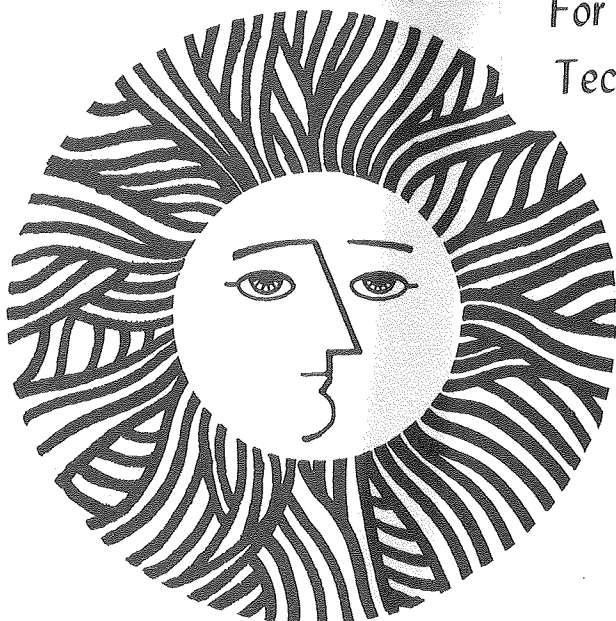
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Donald Lucas and Nancy J. Brown

October 1981

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THE INFLUENCE OF FUEL SULFUR ON THE SELECTIVE REDUCTION  
OF NO BY NH<sub>3</sub>

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## ABSTRACT

The selective reduction of NO by NH<sub>3</sub> addition has been studied in a lean-burning oil fired laboratory combustion tunnel with pyridine and thiophene added to the fuel oil. Two distinct, but interrelated effects were observed. The conversion of a fixed amount of fuel nitrogen to NO in the flame increased as the fuel sulfur concentration increased. In the post-combustion gases, there was a shift in the temperature dependence of the reduction process when the sulfur combustion products were present. The extent of the NO reduction was not significantly altered, but the optimum temperature for reduction shifted to higher values as the sulfur concentration increased.

## INTRODUCTION

More intensive regulations of the emissions of nitrogen oxides from stationary combustion sources have prompted the innovation and characterization of new control technologies suitable for applications in utilities. Previously employed technologies were largely based upon the prevention of thermal NO formation, and these are often ineffective in preventing the formations of fuel NO since the two mechanisms depend differently on experimental combustion conditions.

One of the more recent and attractive abatement technologies is the "Thermal DeNO<sub>x</sub>"<sup>1</sup> process which has been described by Lyon and Longwell<sup>2</sup>. This process removes NO by selectively reducing it with NH<sub>3</sub> added to the post-combustion gases containing excess oxygen. This process is thus independent of the NO formation mechanism and makes no distinction between thermal and fuel NO.

Characterization of the selective reduction of NO through reaction with NH<sub>3</sub>, added to the post-combustion environment, has involved different types of investigations which provide complementary information. Kinetic studies have been undertaken in a quartz flow reactor by Lyon and co-workers<sup>3-5</sup> to elucidate mechanistic details of the NH<sub>3</sub>/NO/O<sub>2</sub> reactions. A recent kinetic modelling study has been undertaken by Miller et al.<sup>6</sup> who were successful in explaining many of the important features of the reactions of NH<sub>3</sub>/NO/O<sub>2</sub> in the post-combustion environment. Muzio

et al.<sup>7,8</sup> investigated the selective reduction process for natural gas, a light oil and several types of coal, and have provided some mechanistic information and determined optimum conditions for maximizing the reduction of NO. Fenimore<sup>9</sup> also has studied the reduction in lean burnt gases, and calculated ultimate reduction limits and some reaction rates.

Research concerned with the effect of sulfur chemistry on the selective reduction has been inconclusive, and in general relatively little research effort has been directed toward investigating the coupling between nitrogen and sulfur combustion chemistry. Wendt et al.<sup>10</sup> and DeSoete<sup>11</sup> have measured fuel nitrogen conversion yields for fuels admixed with sulfur compounds, and found that the presence of fuel sulfur could have a large influence on NO formation.

Our present study is concerned with characterizing the selective reduction process for light distillate oil fuel admixed with variable amounts of pyridene and thiophene in a laboratory scale combustion tunnel under a variety of experimental conditions. This paper will report on those aspects of the study concerned with the investigation of possible synergistic effects between the sulfur and selective reduction chemistry. This is important since some of our remaining fossil fuels have relatively high concentrations of both organically bound sulfur and nitrogen.



## EXPERIMENTAL APPARATUS

The laboratory scale atmospheric pressure combustion tunnel used in this study is described in detail elsewhere.<sup>12</sup> The main sections of the tunnel are constructed from 5 cm inside diameter low alloy steel tube, with combustion of the oil occurring in a 10 cm diameter section. The fuel is #1 diesel oil from the Shell Oil Company with a measured hydrogen/carbon ratio of 1.85, 0.04% by weight sulfur, and less than 0.1% by weight nitrogen. Higher concentrations of fuel nitrogen and sulfur are obtained by adding known amounts of pyridine and thiophene, respectively, to the fuel oil delivery tank. The oil is sprayed into the air flow through a commercial high pressure atomizing nozzle (Monarch Type R, 30° radius, 0.05 l/min). Rapid mixing of the fuel/air mixture was aided by the use of perforated and blocking discs upstream of the nozzle, and by packing the air supply lines with steel wool. Swirl introduced into the air supply was found to be detrimental to the combustion as evidenced by increased flame length and greater sooting tendencies. A quartz tube at the end of the combustion section allows visual inspection of the flame to confirm that the visible flame front terminates at least 50 cm upstream of the ammonia addition section.

Ammonia (Matheson CP grade)/nitrogen mixtures are mixed into the combustion products through four symmetrically oriented uncooled quartz injectors. The heavily insulated reaction and sampling section begins immediately downstream of the injectors

and extends for  $\sim 60$  cm, where it joins the laboratory exhaust system. There are four different axial locations at which quartz microprobes and/or Chromel/Alumel thermocouples may be inserted to a desired radial location. An aspirated thermocouple is used to correct all reported temperatures for radiation losses. Complete combustion and thorough mixing of the product gases are confirmed by measuring temperature and composition profiles in the reaction region when no ammonia is added. Various analytical techniques are used to measure species concentrations, including chemiluminescent analyzers ( $\text{NO}$ ,  $\text{NO}_x$ ), fluorescence detection ( $\text{SO}_2$ ), NDIR ( $\text{CO}$ ,  $\text{CO}_2$ ), GC (various species), and wet chemical methods ( $\text{NH}_3$ ). At the reactant velocities normally used, about 17 m/sec, an axial temperature gradient of 1 K/cm was observed. Radial temperature gradients of 20-25 K were measured when the thermocouple was moved from the centerline position to one 80% of the distance to the combustor wall. Concentrations of  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{NO}$  were found to be independent of probe position, with the  $\text{CO}$  and  $\text{CO}_2$  measurements within experimental error of their expected values. Mixing characteristics of the ammonia injectors were determined by introducing  $\text{NO}$  through the injector system and then measuring the  $\text{NO}$  radial and axial profiles downstream. It was found that mixing was essentially complete within 20 cm from the injection site. Concentration profiles of  $\text{NO}$  and  $\text{NH}_3$  measured when reduction occurs indicate that the reaction is essentially finished (>95%) by the final probe station. The data presented in this study are from the centerline position of the final probe position, 59 cm downstream of the ammonia injection site.

## RESULTS

The reduction of NO by NH<sub>3</sub> addition to the post-combustion gases has been measured as a function of temperature, added NH<sub>3</sub> concentration, and concentration of fuel sulfur. The equivalence ratio in this study was held fixed at a  $\phi = 0.89$ . Fuel nitrogen was also held constant at 1.02% by weight through the volumetric addition of pyridine to the fuel oil. Selected samples were analyzed by the Microchemical Analysis Laboratory of the University of California at Berkeley. Complete conversion of the fuel nitrogen to NO would result in an NO concentration of ~1200 ppm in the exhaust gases. The actual measured concentration before reaction with NH<sub>3</sub> is termed  $[NO]_i$ . The temperatures listed, T\* values, are measured at the centerline immediately upstream of the ammonia injectors. The relative amount of ammonia added is defined by  $\beta = [NH_3]_i / [NO]_i$ .

Prior to determining the effect of fuel sulfur on the NH<sub>3</sub> reduction process, the conversion of fuel nitrogen to NO was measured as a function of fuel sulfur concentration. Table I lists these results for three different fuel sulfur concentrations and various T\* values. With no pyridine added to the fuel thermal NO concentrations of 40-45 ppm were measured. The thermal concentration was subtracted from the  $[NO]_i$  values

when calculating the fuel nitrogen conversion efficiency. The addition of fuel sulfur tends to increase the amount of NO formed from a fixed amount of fuel nitrogen, with more NO formed as the concentration of thiophene increases. As might be expected, the formation of NO does not have a strong dependence on  $T^*$ , which is measured well downstream of the flame. However, because  $T^*$  is controlled by cooling of the combustor around the flame zone it was necessary to determine that this control did not effect the flame conditions. Measured  $SO_2$  concentrations indicate that within experimental error, quantitative conversion of the fuel sulfur occurs when no  $NH_3$  is present. However, when both sulfur compounds and  $NH_3$  are present, serious errors in the measurements of both species are caused from the formation of sulfur-ammonia species which most likely occurs at the lower temperatures in the probes, sampling lines, or analyzers.

The temperature dependence of the reduction process for various fuel sulfur concentrations is shown in the first three figures. Nitric oxide concentrations are normalized to the initial NO levels measured. Figure 1 illustrates the temperature dependence when no thiophene is added to the fuel. As more ammonia is added (increasing  $\beta$ ), greater reduction of NO is obtained. Also, the optimum temperature for reduction increases with increasing  $\beta$ . The effect of increasing the fuel sulfur is shown in Figures 2 and 3. There is a noticeable shift to higher optimum temperatures when the fuel sulfur increases. However,

while the temperature at which the optimum reduction occurs does change, the maximum amount of reduction for a given  $\beta$  is essentially unchanged. A plot of NO reduction as a function of  $\beta$  at a fixed temperature is shown in Figure 4. At  $\beta$  values less than 1, the fuel sulfur has little effect on the reduction process. Above  $\beta=1$  the change in the reduction process with increasing fuel sulfur at a constant temperature is more obvious. Preliminary results indicate that this trend continues at even higher fuel sulfur concentrations.

#### DISCUSSION

The presence of fuel sulfur has two different, though interrelated manifestations: there is an increase in the conversion of fuel nitrogen to NO as the fuel is burned, and the optimum temperature for the  $\text{NH}_3$  reduction process shifts to higher values. The observed increase in NO production in the presence of fuel sulfur is in agreement with the results of Wendt et al.<sup>9</sup>, who added thiophene to rich turbulent diffusion flames doped with  $\text{NH}_3$  or pyridine. They showed that the burning characteristics of the fuel oil were not affected by the addition of an aromatic fuel additive in low concentrations but rather by the presence of organic sulfur by doping the fuel with benzene in place of thiophene. They reported NO production to be quite dependent on the method of mixing the fuel and air, with more NO produced in the less turbulent diffusion flames. It is very

difficult, however, to quantitatively characterize "mixing" in a turbulent diffusion flame. In our study the flow conditions were held constant, and there were no visible differences in the flames when thiophene was present. The addition of thiophene changes the equivalence ratio only slightly, less than the uncertainty introduced by the fuel and air metering systems. It was previously found that for this experimental configuration the fuel NO levels had only a mild dependence on the equivalence ratio for the value used in this study<sup>12</sup>. Since we have made no attempt to observe reaction intermediates during the combustion of fuel nitrogen, we can only speculate as to the cause of the increased NO formation.

The dependence of the selective reduction of NO by NH<sub>3</sub> on temperature and  $\beta$  has been reported previously<sup>7,8</sup>. When no thiophene is added to the pyridine/oil mixture (0.04% fuel sulfur) the results in terms of NO reduction are essentially identical to those obtained when NO is injected in the air supply (replacing the pyridine in the fuel) to produce a downstream NO concentration of 500ppm<sup>12</sup>. It should be remembered that the reduction process takes place in homogeneous, lean mixtures of post-combustion gases at temperatures well below those encountered in the flame. Sulfur compounds in the post-combustion gases could affect the reduction process by reacting with the ammonia or an ammonia derived species, effectively lowering the concentration of the reducing agent (lower  $\beta$ ). This would result in less NO reduction and in a decrease in the

temperature for achieving the optimum NO reduction. Neither of these is observed. Lower concentrations of SO<sub>2</sub> and NH<sub>3</sub> are measured when both species are present, but this is most likely attributable to reactions in the sampling system. The observed shift in the optimum temperature suggests a change in the reaction pathway when sulfur compounds are present. One possibility is the existence of fuel-rich pockets immediately around the ammonia injectors: the added ammonia can cause the mixture to become locally rich, reducing the SO<sub>2</sub> to other species such as SH, SO, or H<sub>2</sub>S, thereby altering the NH<sub>i</sub> (i=0,1,2,or3) concentration profiles and the temperature dependence of the reduction process. Alternatively, the sulfur species themselves could react with the NO or NH<sub>i</sub> species present. Sulfur dioxide has been identified as the major product of the combustion of sulfur species in lean environments; however, other sulfur species present in significantly smaller concentrations could also be important.

A significant shift in the optimum temperature for the reduction process has been observed previously by Muzio et al.<sup>8</sup> when using pulverized coal as the fuel. The high sulfur content coals were found to have a higher optimum temperature for NO reduction than the lower sulfur content coals. However, because of the many variables involved in the experiment it was not possible to identify the sulfur as being the sole cause of the temperature shift. Additional research is warranted to further elucidate the role of various sulfur compounds in nitrogen combustion chemistry.

## ACKNOWLEDGEMENTS

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TABLE I

$\frac{T}{K}^*$	FUEL S <sup>a</sup> %	[SO <sub>2</sub> ]i <sup>b</sup> ppm	[NO]i <sup>c</sup> ppm	% FUEL N CONVERSION TO NO
1170±5	0.04	--	515±10	40
1188			510	39
1224			520	40
1252			515	40
1282			515	40
1176±5	0.33	148±15	610±10	48
1200			600	47
1230			615	48
1268			627	49
1293			650	51
1167±5	0.63	--	675±15	53
1194			670	53
1245			705	55

FIGURE CAPTIONS

FIGURE 1. NO reduction as a function of temperature with no thiophene added to fuel (0.04% fuel S).

FIGURE 2. NO reduction with thiophene addition (0.33% fuel S).

FIGURE 3. NO reduction with thiophene addition (0.63% fuel S).

FIGURE 4. NO reduction at a constant temperature as a function of added  $\text{NH}_3$ .

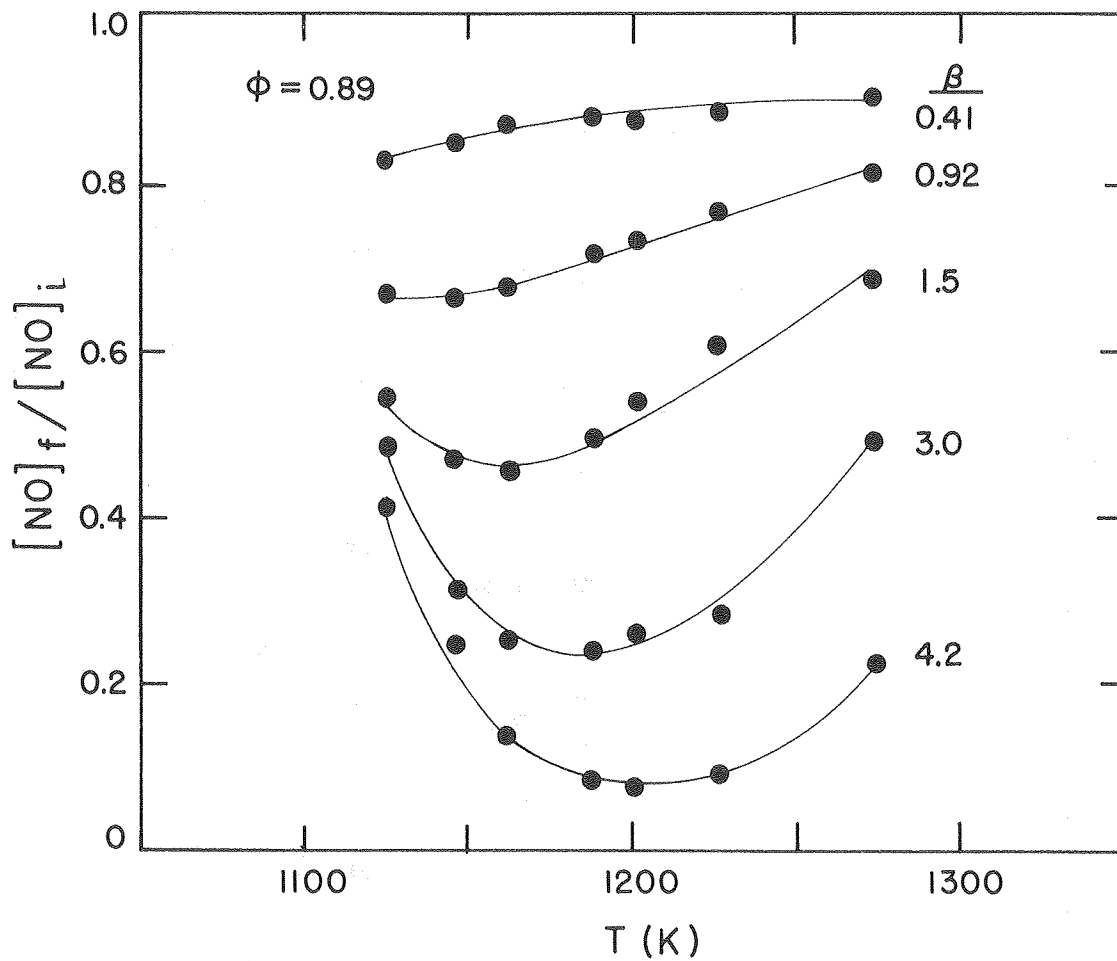


Figure 1

XBL 812-8279

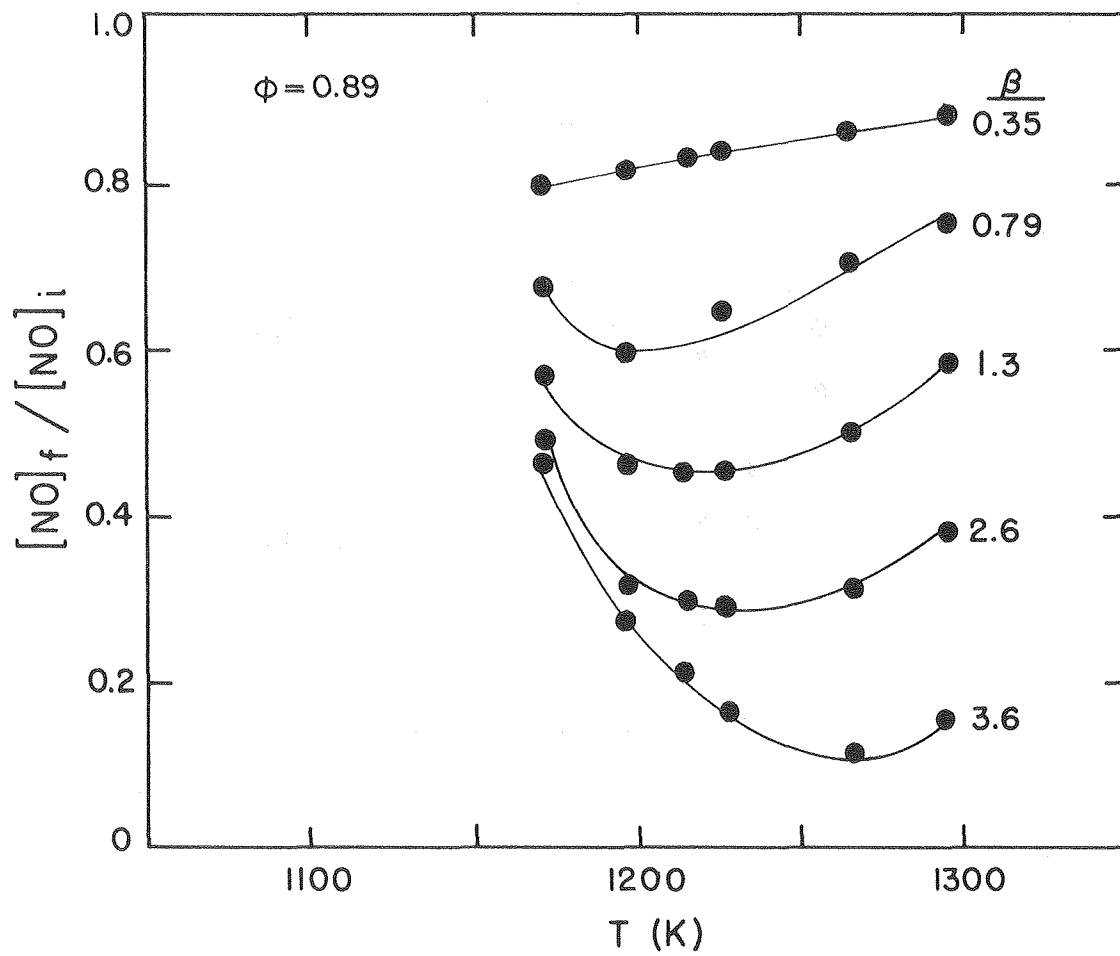


Figure 2

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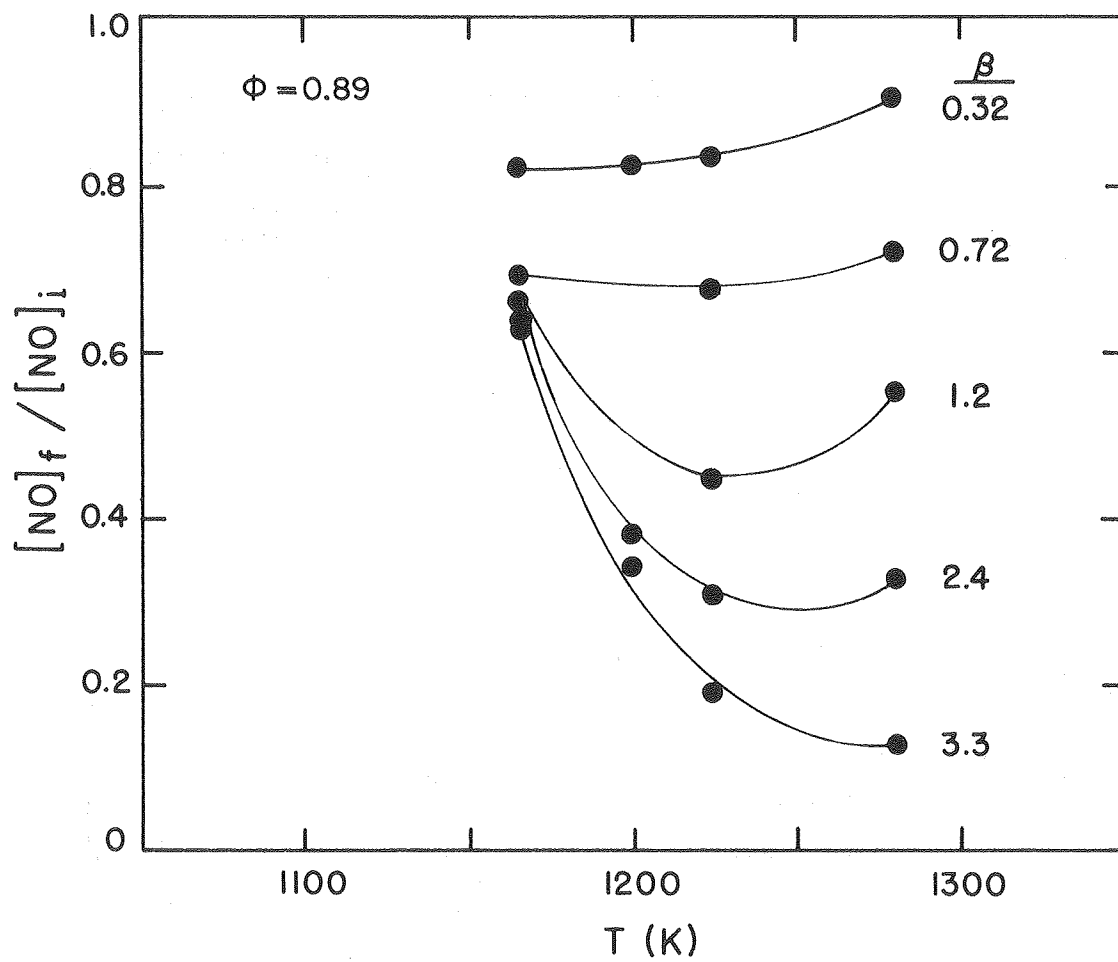


Figure 3

XBL 812-8278

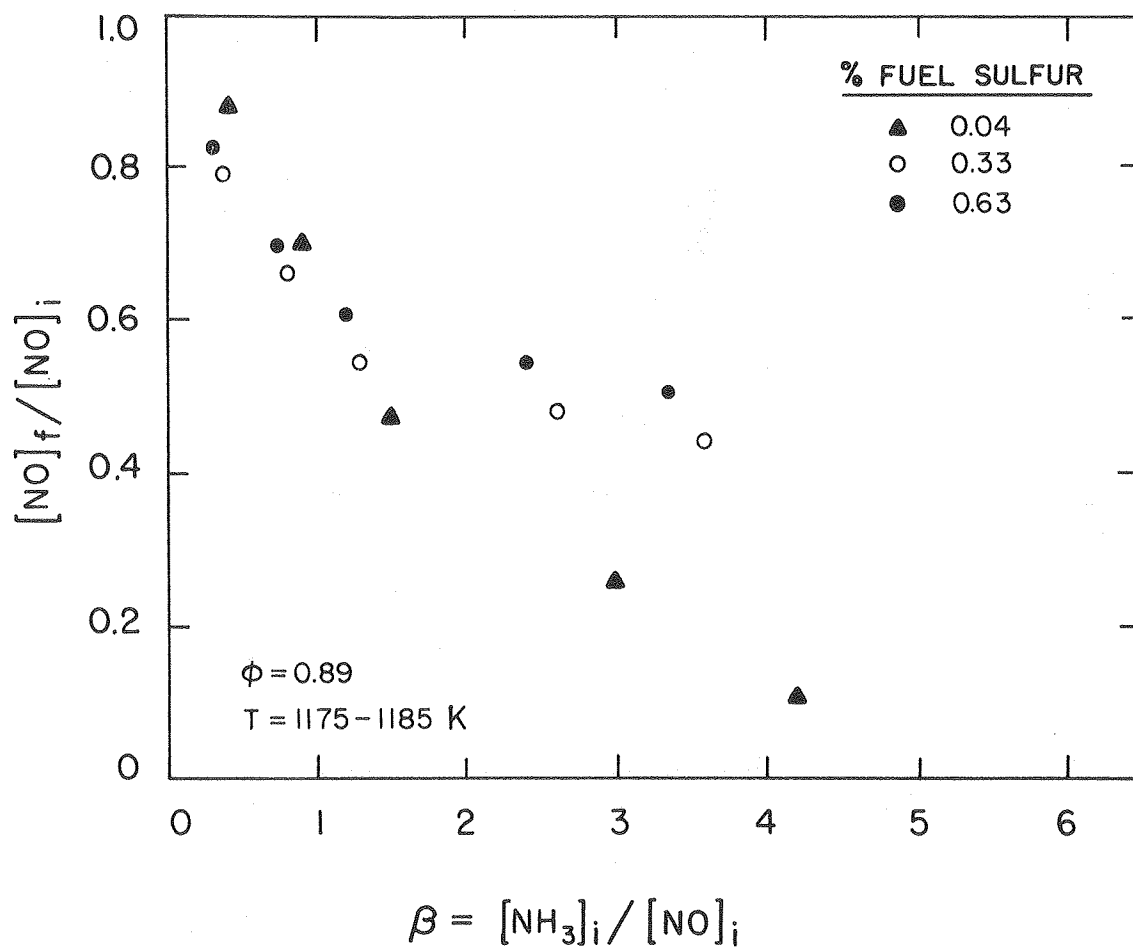


Figure 4

XBL 812-8280