STATUS OF NO_x CONTROL FOR COAL-FIRED POWER PLANTS

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ABSTRACT

The status of technologies for controlling emissions of oxides of nitrogen (NO_x) from coal-fired power plants is reviewed. A discussion of current technology as well as future NO_x control approaches is presented. Included in this latter category are advanced combustion approaches as well as post-combustion alternatives such as catalytic and non catalytic ammonia-based systems and wet scrubbing. Special emphasis is given to unresolved development issues as they relate to practical applications on coal-fired power plants.

I. INTRODUCTION

Oxides of nitrogen are a subject of general interest in California and of particular interest in Southern California. In this paper the various control technology options available for power plant applications are discussed. The discussion is primarily oriented around direct pulverized coal utilization, though much of what will be said applies to other combustion devices and fuels as well.

II. BACKGROUND

Oxides of nitrogen from combustion sources are composed of nitric oxide (NO) and nitrogen dioxide (NO_2). Together they are referred to as NO_x. From an effects standpoint, it is mainly the NO_2 and its derivatives which are of concern. However, from a control technology standpoint, it is the NO which is of interest since the majority of the direct emissions of NO_x from power plants are in this form.

There are two sources of nitrogen which can lead to NO_x formation. The first is molecular nitrogen (N_2) carried along with the oxygen in the air. At high combustion temperatures this normally inert N_2 can react with oxygen to form NO_x. Since this occurs at high temperature, it is frequently referred to as thermal NO_x. Control of NO_x from this nitrogen source is reasonably well established technology. The other source of nitrogen is that inherently bound within fuel molecules. Because earlier thermal NO_x control measures are relatively ineffective for this nitrogen source, it is the inherent nitrogen which makes NO_x control difficult on any fuel containing significant quantities of nitrogen. Coal falls into this category since it typically contains 1 to 1-1/2% nitrogen by weight.

III. CURRENT TECHNOLOGY

At the present time, operational modifications to the combustion process are the only commercially available means of controlling NO_x emissions from coal-fired power plants (Table I). This usually involves some form of staged combustion (NO_x ports, overfire air ports, burners out of service) or low NO_x burners both of which are aimed at minimizing the quantity of oxygen available for combination with air or fuel nitrogen sources. Combustion techniques specifically aimed at reducing thermal NO_x (flue gas recirculation, reduced air preheat, water injection) are relatively ineffective when applied to coal-fired boilers.

Considerable testing of coal-fired boilers, mainly by EPA, has shown that current regulations of 0.7 lb/10^6Btu (about 500 ppm for coal) can be achieved. However, from an operating standpoint, significant questions regarding boiler corrosion and slagging are still unanswered. EPA has proposed that the standard be lowered to 0.6 lb/10^6Btu. This has prompted considerable discussion, since the ability to reliably meet the 0.7 lb/10^6Btu standard still has not been proven.

Currently, boiler manufacturers are investigating burner techniques for controlling NO_x to 0.6 lb/10^6Btu and lower levels. However, the ability to meet these levels is unknown, as are long-term reliability issues similar to those discussed above.

Emissions in the 250-300 ppm range have been reported in one Japanese coal-fired installation. This has been accomplished through advanced burner designs and staged combustion. Long-term reliability issues have not been released.

IV. ADVANCED TECHNOLOGY

Reduction in emissions beyond the levels cited above will require innovative new technologies. Both advanced combustion process techniques as well as post-combustion approaches such as catalysis or scrubbing are currently under investigation.

A. COMBUSTION MODIFICATION

There is a considerable body of basic data indicating that nitrogen in coal can be prevented from forming NO_x by manipulating the combustion process. Properly done, the nitrogen in the fuel can be reduced to harmless molecular nitrogen.

The fundamental requirement to accomplish the desired effect is through combustion under controlled reducing conditions. One such approach to this problem is shown in Fig. 1. Pulverized coal is introduced into a burner with less air than required for complete combustion. A key feature of this approach is the physical isolation of the reducing zone from the oxidizing zone, which permits accurate control of process stoichiometry. The extended length of the combustor provides the necessary residence time to partially oxidize the coal and permit desirable N_2-forming reactions to occur. Heat removal also occurs along the combustor to avoid slagging and for process temperature control. Secondary air is added at the exit of the extended furnace to bring the combustion products to oxidizing conditions for the balance of their passage through conventional steam generating equipment.

Development of this process is being conducted at two scales. Preliminary screening tests are being done at approximately 4 x 10^6 Btu/hr (0.4 MW). Prototype development will then be done at 50 x 10^6 Btu/hr (5 MW).

Results of this research are only now becoming available. Typical results from the 4 x 10^6 Btu/hr scale give about 150 ppm for a typical western subbituminous coal. While extrapolation of experience at the laboratory scale to full-scale burners (typically on the order of 200 x 10^6 Btu/hr) must be approached with caution, the results to date must be viewed as encouraging. Considerably more research into scale-up effects, slagging, corrosion, safety, and general operability-reliability aspects will be required. Commercial availability is scheduled for the early to mid 1980s time frame. Preliminary cost estimates for the low NO_x combustion system are estimated at about $5/kW for new installations.

B. POST-COMBUSTION CONTROL TECHNIQUES

Even if the advanced combustion techniques are 100% successful, it is unlikely that NO_x below the 100-200 ppm range can be achieved. If emissions below this level are deemed necessary, post-combustion processes will probably be required.

Post-combustion systems fall into two major categories: dry ammonia (NH_3) based and wet scrubbing. The NH_3 systems are further broken down into catalytic and non-catalytic technologies. Some dry systems can be used to collect NO_x and SO_x. The wet scrubbing systems can be used for NO_x alone, but almost always involve simultaneous NO_x and SO_x removal for economic reasons. However, comparatively little work has been done on wet scrubbing relative to dry processes. For both NH_3 and scrubbing processes, the vast majority of work has been done in Japan, where stringent NO_x standards have been imposed.

1. Catalytic NO_x Control with NH_3

Catalytic reduction of NO_x with ammonia (NH_3) is selective; that is, NH_3 preferentially reacts with NO_x over other compounds according to the following hypothesized overall reactions:

$$4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O \quad (1)$$
$$4NH_3 + 2NO_2 + O_2 \rightarrow 3N_2 + 6H_2O \quad (2)$$

As can be seen, only gaseous N_2 and H_2O are the theoretical products.

A schematic diagram of a typical catalyst application in a coal-fired boiler is shown in Fig. 2. The catalyst is physically located between the boiler economizer and the air preheater. Such a location is necessary since required catalyst process temperatures are in the 700-800°F range. As can be seen, the catalytic system involves reactors and ductwork of significant size. A graph of the NO_x removal efficiency as a function of temperature for a typical catalytic system is shown in Fig. 3. Reheat of the flue gas downstream of the air preheater to provide these temperatures is viewed as impractical.

In Japan, a significant number of catalytic processes have been investigated on flue gas from natural gas and oil-fired boilers, and NO_x reductions of 90% have been reported. However, only limited data are available for flue gas having SO_2 and particulate levels characteristic of U.S. coal-fired applications. Acknowledged research to date has only been at the several hundred cfm (0.1 MW) to several thousand cfm (1 MW) scale.

In addition to the basic question of scale-up, there are several key development issues which remain to be solved regarding catalytic NO_x removal. Table II summarizes these issues, along with the [illegible]ical problems that are created, potential solutions, and a qualitative estimate of costs.

a. Dust Tolerance

One major development issue is related to the quantity of fly ash associated with coal. Particulate load in coal-fired boiler gases is about 1000 times that for oil. This means that conventional packed bed contacting designs are not practical, since they would physically plug up.

A solution to the dust problem can be addressed from two standpoints: elimination of the fly ash by using a hot electrostatic precipitator upstream of the catalyst; or development of dust-tolerant contacting geometries. In practice a dust-tolerant catalyst is probably required in any event because precipitator/boiler operating upsets which produce transient particulate concentrations cannot be completely eliminated.

Research into catalyst contactor configurations which are tolerant of full coal-fired dust concentrations has begun in Japan. While some schemes involve moving beds, the more promising approaches use what is frequently termed a parallel passage reactor. In such a contactor the reactor walls are oriented parallel to the direction of flow. This permits diffusion of the NO_x and NH_3 to the active catalyst sites at the walls, while the dust particles continue flowing with the bulk gases. Parallel passage reactor configurations under investigation include pipe, honeycomb and corrugated. Because of the competitive nature of these developments, only limited public information is now available regarding details of the time-dependent performance of these devices over catalyst lives of commercial interest. The success in achieving erosion and plugging resistant geometries will be known as data is published.

It is worth noting that extrapolation of coal-fired catalyst data to coal, and vice versa, must be approached with caution. In addition to the differences in particulate loadings noted earlier, the fly ash chemical composition (carbon, trace elements, and acidity) and physical characteristics ("stickiness") are also quite different between the two fuels.

Another problem which must be addressed even in a parallel passage reactor is the problem of physical blockage of the small openings of the reactor. It may be necessary to provide some form of particulate removal -- such as an impaction plate or cyclone -- to prevent impingement of large fly ash agglomerates on the catalyst. The requirement of such a device would obviously increase the costs of the catalytic system.

b. NH_3 Carryover

Another significant problem that must be successfully resolved before catalytic systems can be viewed as applicable to coal-fired boilers relates to the carryover of unreacted NH_3 from the catalyst. In addition to being an undesirable emission by itself, NH_3 can react with SO_3 to form sulfates or bisulfates which could also be emitted to the atmosphere. From a utility operating standpoint, an even more pressing problem is the formation, condensation and subsequent deposition of ammonium bisulfate on low-temperature heat recovery components downstream of the catalytic reactor.

Deposition of this material is undesirable since it will result in increasing pressure drop leading to subsequent reduction in the generating capacity of the plant. The material is also suspected to be corrosive.

An equilibrium graph showing the temperature dependence of bisulfate formation as a function of SO_3, H_2O and NH_3 is illustrated in Fig. 4.

Prevention of bisulfate deposition may be accomplished via lowered NH_3/NO stoichiometries (which lowers NO_x removal), or a catalyst which decomposes NH_3. At least one Japanese company is researching an NH_3 decomposition catalyst.

c. Low Load Operation

Bisulfate deposition can also be a problem within the catalytic reactor itself when temperatures drop below the condensation point such as occurs at low load operation. Potential solutions include maintaining the catalyst at temperatures above the bisulfate point by incorporating high temperature flue gas bypass or higher catalyst operating temperatures. The effectiveness of the catalysts at higher temperatures is not known.

d. Automatic Control System

Another engineering problem which requires attention is the ammonia injection control system. Japanese systems typically use feed forward control only based on inputs from oil-fuel flow, O_2 concentration and inlet NO_x. Environmental, economic and operating considerations in U.S. applications will probably dictate that the control system additionally incorporate as a minimum a feedback loop based on reactor outlet NH_3 and NO_x.

e. Environmental Issues

One final point should be noted. Since the objective of any catalytic NO_x process is to improve the environment, care must be taken to assure that potentially undesirable byproducts are not released in the process. In addition to NH_3, ammonium sulfate and bisulfate mentioned earlier, emissions of N_2O (the result of incomplete reduction of NO_x), SO_3 (caused by oxidation of SO_2 over base metal catalysts), amines and other compounds have yet to be evaluated.

On the basis of personal discussions with Japanese vendors, economics range from $10-80/kW, averaging $30/kW. However, in many cases it is not clear whether this cost covers equipment only or installation. It almost certainly does not include IDC, G&A and other owner overheads. Besides these basic questions and those which always exist when extrapolating limited pilot plant data to commercial applications, there are other factors which confuse the cost picture. For example, differences in labor rates and productivity and raw material costs between Japan and the U.S. make it difficult to accurately judge costs by simply converting from yen to dollar at the current exchange rate. Other factors could also lead to substantially different costs, such as OSHA requirements and general operating philosophy. EPRI currently has projects aimed at accurately defining the cost of catalytic technology for U.S. power plant applications. This information is expected to be available later this year.

Current research activity on catalytic NO_x systems is at a fairly low level. EPA has just awarded a contract to a Japanese vendor for research on a 1/2 MW pilot plant. EPRI intends to perform research at the 2-1/2 MW scale. Discussions with vendors are currently under way. A major feature of this research will be the systematic investigation of the major development issues noted earlier.

2. Non-Catalytic NO_x Control with NH_3

In addition to the catalytic systems, research is also underway on noncatalytic NH_3-based NO_x control technology. Conceptually, the noncatalytic system is attractive; all that is required is NH_3 and an injection system. The catalyst is eliminated. NH_3 is injected at the proper temperature and the NO_x and NH_3 selectively and homogeneously react, probably according to equations 1 and 2. The relatively narrow temperature range over which the process is effective is seen in Fig. 5 for an oil-fired laboratory experiment. This narrow temperature range makes it somewhat difficult to apply the technique, since the temperature at a single point in a boiler can vary significantly with fuel fluctuations, ash deposits, operating conditions, and load. Solutions to the temperature sensitivity problem include multiple injection sites, moveable injection probes or hydrogen addition. The likelihood of this latter technique in utility applications is not well defined.

The most significant application to date of the noncatalytic technology is the 375 MW full-scale installation at the oil-fired Chita plant of Chubu Electric in Japan (Fig. 6). This unit uses multiple injection sites to provide temperature variation flexibility. The NO_x reduction, NH_3/NO ratio, and NH_3 carry-over are shown in Figs. 7 and 8 as a function of load. The unique shape of the curves with load is due to temperature variations with load and the use of two NH_3 injection points. NH_3 carry-over is high especially at low load and may limit the NO_x reduction in U.S. applications.

Air preheater deposition at Chita has not been a problem due to the low (1-2 ppm) SO_3 levels associated with the 0.2% S oil used. Feed forward control based on oil flow, inlet NO_x, and excess

O_2 is used. As with the catalytic approach, U.S. utility operating practices will probably dictate the addition of a feedback loop as well.

The currently available data for coal firing is shown in Fig. 9. These data were obtained on a 3 x 10^6Btu/hr laboratory facility. The variation in optimum process temperature with unidentified coal and/or ash characteristics shown may complicate the ease of practical application.

The noncatalytic technique has removal efficiencies which are lower than the catalytic approach, higher NH_3 consumption, and higher NH_3 carry-over. Problems associated with NH_3 carry-over have already been discussed and need not be repeated.

3. NO_x Scrubbing

Control of NO_x in a scrubbing process is attractive because potentially two emissions of concern (NO_x and SO_2) can be controlled simultaneously. However, scrubbing of NO_x is limited by the insolubility of NO in most scrubber liquors.

Two general approaches have been devised to get around the NO insolubility problem: conversion of the NO to more soluble species and use of an NO "getter" in the scrubber liquor.

Oxidation of NO has been explored with hypochlorite and O_3. However, because of water quality considerations, only O_3 is of interest. However, O_3 production is expensive and energy-intensive. In addition, the oxygenated NO_x is not that soluble and large vessels and/or large liquid-to-gas flow rates are required to perform absorption. As an alternative to extremely large vessels and L/G's, the addition of catalysts has been considered. For the typical flowsheet shown in Fig. 10, $CuCl_2$ and NaCl are used. Both of these materials again raise questions of water quality. Additional water quality concerns relate to potential byproducts of the process, such as imododisulfonate and dithionate. Consideration of these factors has led at least one research organization in Japan to halt further development.

The other major category of wet processes involves the use of ethylene diamine tetraacetic acid (EDTA) to form reactive adducts with NO. The process flowsheet is shown in Fig. 11. These processes also form potentially undesirable byproducts similar to those in the O_3 system. The major development issue in wet systems is regeneration of the EDTA. A viable approach has not yet been reported.

Even if the issues noted above can be overcome, there is one overriding consideration which must be addressed. This relates to the feasibility of the process on low-sulfur coals. Reduction of the NO via EDTA or O_3 occurs through reaction with sulfite ion which is inherently low on scrubbers applied to low-sulfur coal. It is postulated that an SO_2/NO_x ratio of greater than 2-1/2:1 must exist to effect the process chemistry. Typical western coals are on the order of 1:1 or 2:1. These ratios could make for low NO_x removal efficiencies. Alternatively, $SO_3^=$ reagents could be added, but this is viewed as economically unattractive.

V. CONCLUSIONS

Development of NO_x control technology for coal-fired power plants at the pilot plant scale is just now beginning in the U.S. Direct extrapolation of Japanese experience both economically and technically should be approached with caution.

The most cost-effective solution to NO_x control will continue to be combustion modification. If greater control than can be provided by combustion control is necessary, NH_3-based systems have an advantage over scrubbing systems, although considerable technical hurdles are yet to be resolved.

Table I

CURRENT NO_x TECHNOLOGY

Modification	*NO_x Level PPM*	*Unresolved Issues*
• Operational Combustion Changes	• 550	• Corrosion, Slagging, Byproduct Emissions
• New Burners	• Below 550	• Corrosion, Slagging, Byproduct Emissions, Effect of Coal Type
• Reported Japanese Data	• 250 - 300	• Accuracy of Data Unknown

Table II

CATALYTIC NO_x CONTROL

Development Issue	*Practical Problem*	*Potential Solutions*	*Qualitative Cost Impact*
• Dust Loading	• Catalyst Bed Pluggage/Ero[illegible]n	• Parallel Passage Reactor with Inertial Separator	• Large
		• Hot Electrostatic Precipitator	• Large (possibly impractical)
• NH_3 Carryover	• Environmental Emissions	• NH_3 Decomposition Catalyst	• Large
	• Air Heate[illegible] Deposition/ Corrosion	• Lower NH_3 Feed (lowers NO_x removal)	• Small

Table II (Contd)

CATALYTIC NO_x CONTROL (continued)

Development Issue	*Practical Problem*	*Potential Solutions*	*Qualitative Cost Impact*
• Low Load Operation	• Catalyst Pluggage	• Economizer Bypass	• Large
		• High Temperature Catalyst	• Large
• Automat[illegible] Contr[illegible]	[illegible] NH_3	• Feedback Control	• Small
• Bypr[illegible] Em[illegible]		• [illegible]nknown	• Unknown

CONCEPTUAL APPLICATION OF EPRI/B&W LOW NO_x COMBUSTOR

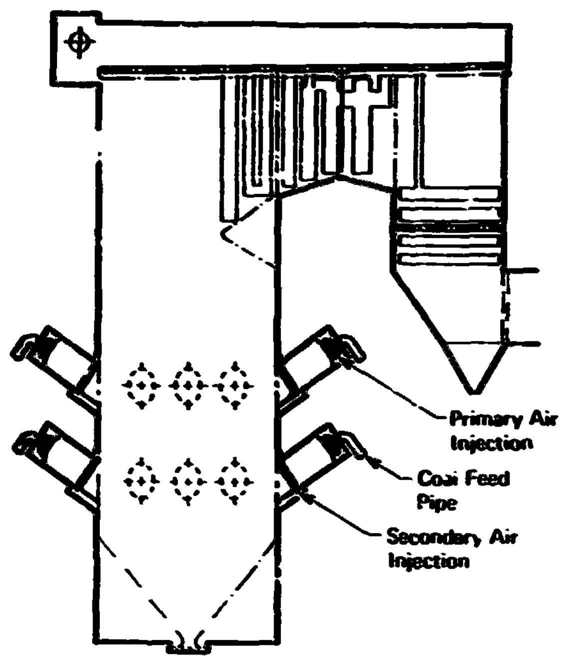

Figure 1

CATALYTIC NO_x APPLICATION TO COAL-FIRED PLANT

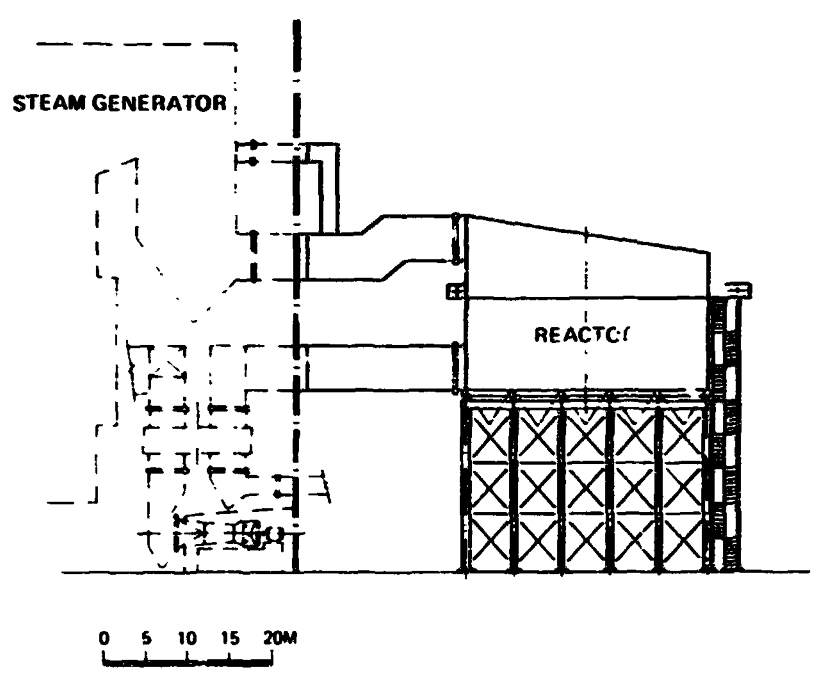

Figure 2

NO_x REMOVAL VS TEMPERATURE CATALYTIC NO_x SYSTEM

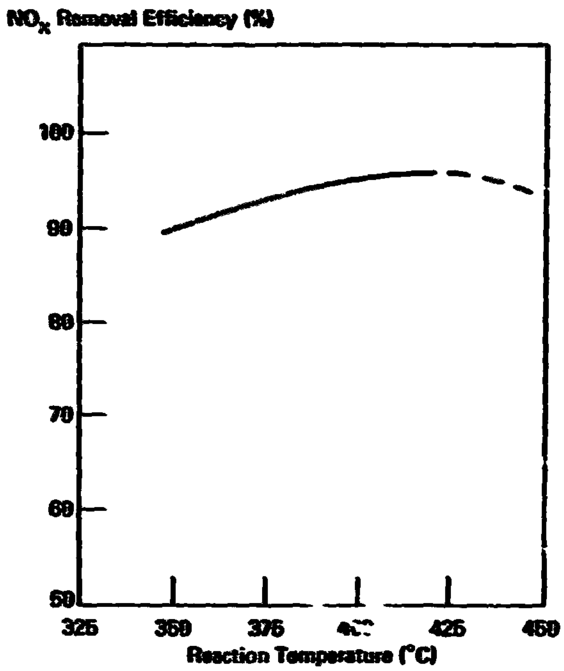

Figure 3

FORMATION TEMPERATURE OF NH_4HSO_4

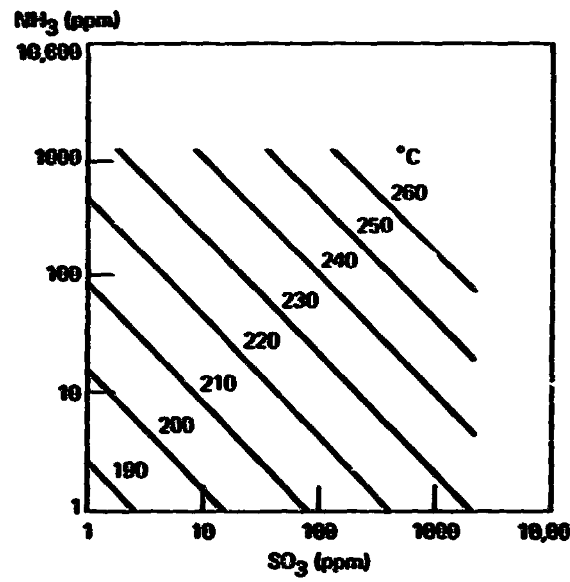

Figure 4

OIL-FIRED NO REDUCTIONS WITH NONCATALYTIC AMMONIA INJECTION LABORATORY DATA

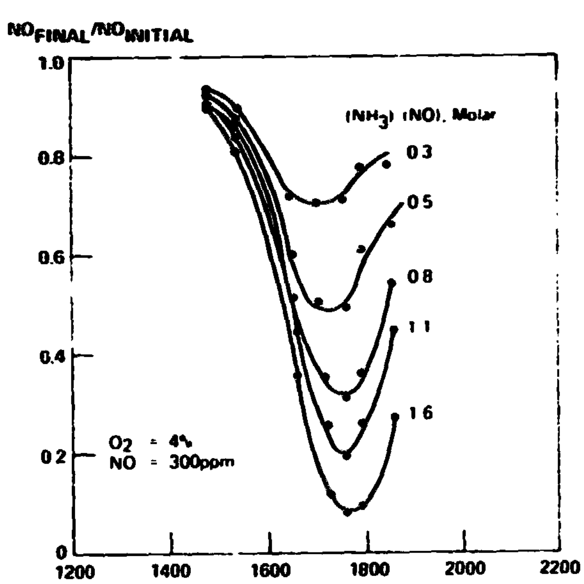

Figure 5