N₂O FORMATION IN COMBUSTION SYSTEMS**DISCLAIMER**

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SUMMARY

The objective of this project is to characterize N_2O emissions from combustion sources emphasizing N_2O emissions from post-combustion selective gas phase NO_x reduction processes and reburning. The processes to be evaluated include ammonia, urea and cyanuric acid injection and reburning. The project includes pilot-scale testing at two facilities supported by chemical kinetic modeling. Testing will be performed on both a gas-fired plug flow combustor and a pulverized-coal fired combustor.

Work performed to date has included the performance of the initial detailed chemical kinetics calculations. These calculations showed that both urea and cyanuric acid produce significant quantities of N_2O , while NH_3 injection produced negligible amounts. These kinetics data support limited test results reported for cyanuric acid and ammonia injection.

Laboratory work to evaluate the selective gas phase NO_x reduction processes listed above will begin in the gas-fired facility early in CY 1990. Testing to evaluate reburning at the coal-fired facility is currently planned to be performed in parallel with the testing at the gas-fired facility. Following completion of that work, additional kinetics calculations will be performed.

INTRODUCTION

N_2O is a relatively strong absorber of infrared radiation in the troposphere, and can contribute to the Greenhouse Effect. Once transported to the stratosphere, N_2O is the largest source of stratospheric NO and the major natural chemical sink establishing the stratospheric O_3 concentration (1). The mean global N_2O concentration of approximately 330 ppb has been increasing at a rate of 0.2-0.4 percent per year (2,3).

Increases in atmospheric N_2O concentrations have been attributed to anthropogenic sources, although the dominant man-made source of N_2O is still uncertain. Previous N_2O measurements from combustion sources indicated that substantial levels of N_2O were found in systems fired with residual oil or coals (e.g., fuels containing nitrogen and sulfur). The measurements of Hao

et al. (4) and Castaldini et al. (5) suggest that N_2O levels were 25-40 percent of the NO_x concentration. Global N_2O production from combustion sources was then calculated using the relationship between N_2O and NO_x , coupled with known combustion generated NO_x emissions.

The measurements to establish emission factors for combustion generated N_2O have been made primarily by gas chromatographic analysis of gas samples collected in glass or stainless steel containers. Recent measurements have shown that these grab samples can undergo chemical reaction in their containers, creating N_2O concentrations substantially higher than those originating in the combustion process (6,7). Thus, a sampling "artifact" exists, resulting in the measured N_2O emissions that can exceed actual emissions.

The artifact was discussed by Muzio, et al. (8), and shown to result from reactions between the NO_x , SO_2 and N_2O present in the sample containers. The amount of N_2O formed depends on the amount of SO_2 and water present and the initial NO level. A continuous infrared analyzer, suitable for characterizing N_2O emissions from combustion sources has been used to perform continuous on line N_2O measurements at nine utility boilers. The data indicate that N_2O levels are generally less than 5 ppm, and were not related to the NO_x levels in the flue gas. This work indicates that fossil fuel combustion is not a significant source of N_2O emissions.

Concurrently, Caton and Siebers (9,10) performed laboratory tests characterizing NO_x removals achievable using cyanuric acid. This work showed that up to 90 percent of the NO_x removed was converted to N_2O . Concerns were then raised regarding the performance of currently available post-combustion NO_x reduction processes, including ammonia, urea or cyanuric acid injection. Each process involves the selective gas phase reduction of NO by one of the nitrogen-containing reagents listed above. The current project is investigating N_2O emissions from each of these processes.

The specific objectives of this project are aimed at determining:

- o The extent to which N_2O is formed as a product of selective gas phase reduction processes using ammonia, urea and cyanuric acid.
- o How N_2O formation depends on the following process parameters:

- temperature
  - residence time
  - initial NO_x level
  - reductant type (NH_3 , urea, cyanuric acid)
  - amount of reductant injected
  - background gas composition (O_2 , CO , SO_2)
- o Whether coal ash impacts the process.
  - o In addition to the selective NO_x reduction processes, the program will investigate the effect of reburning on N_2O emissions.

The program involves pilot-scale combustion studies in two facilities coupled with chemical kinetic modeling to guide and analyze the experimental data.

The project is divided into five (5) tasks as listed below. Each task is discussed in the following paragraphs.

- Task 1: Chemical Kinetic Modeling of N_2O Processes
- Task 2: Plug Flow Combustor Tests
- Task 3: Coal Selection
- Task 4: Coal-Fired Combustor Tests
- Task 5: Data Analysis and Reporting

Task 1 includes the chemical kinetic modeling of N_2O processes using a model initially developed by EER for predictions of gas reburning phenomena. The model includes 201 reactions and rate constants. An initial literature review ensured that the model incorporates potential mechanisms covering the gas phase reduction of NO with ammonia, urea and cyanuric acid. The basic tool used to model this system is a one-dimensional kinetics code, which is capable of considering both well-stirred and plug-flow reactors.

Task 2 includes a series of plug-flow combustor tests to investigate parameters that can lead to N_2O formation during the gas phase reduction of NO . This testing will be performed using the Fossil Energy Research Corp. 250,000 Btu/hr down-fired combustion tunnel. The tunnel is fully instrumented to provide temperature and gaseous composition measurements at a number of locations downstream of the burner.

For the current series of tests, natural gas will be doped with NH_3 to control initial NO_x levels. The NO_x reduction reagents will be injected at the throat. These tests will investigate the impact of the following parameters on N_2O formation: temperature; reducing agent; initial NO levels; N/NO_x molar ratio; and the effect of additives on N_2O emissions.

Continuous gas analysis at the combustor exit will be used to determine N_2O formation at nominal residence times of 1 second, for the majority of the tests. For selected tests, axial gaseous samples will be obtained as well as wet chemical samples for NH_3 determinations.

During Task 3, two coals will be selected for use during the coal combustor tests at UCI. It is anticipated that the coals will consist of an eastern bituminous coal and a subbituminous coal. Sufficient quantities of coal will then be obtained and pulverized for the Task 4 testing.

Coal-fired pilot-scale tests will be performed during Task 4 to confirm the results obtained in the natural gas-fired plug flow combustor tests and to investigate N_2O formation during reburning. This series of tests will be performed in UCI's pulverized coal-fired pilot-scale facility. The system incorporates a variable swirl burner capable of generating flame characteristics similar to large-scale systems.

TECHNICAL PROGRESS TO DATE

This section describes the progress made during the third quarter of the project, on a task basis.

Task 1 - Chemical Kinetic Modeling of N₂O Processes.

No work was performed during this quarter on Task 1. The initial kinetic modeling work was completed during the second quarter of the project. The final modeling work is scheduled to be performed following completion of the laboratory tests.

Task 2 - Plug Flow Combustor Tests

The N₂O analyzer was received during this quarter, and has been installed in a stand-alone sample system. A brief series of tests was performed to optimize the liquid urea injection system. It is anticipated that the reagent injection testing will commence early in CY 1990.

Task 3 - Coal Selection

No progress has been made on Task 3 during this quarter.

Task 4 - Coal-Fired Combustor Tests

No additional work was performed on Task 4 during this quarter.

Task 5 - Data Analysis and Reporting.

Task 5 work performed during this quarter has included the preparation of required monthly progress reports, and presentation of a paper at the recent AR&TD Contractors Meeting at Morgantown, West Virginia.

OUTLINE OF WORK PLANNED FOR NEXT REPORTING PERIOD

Task 1 - Chemical Kinetic Modeling of N_2O Processes

No work is planned for this task during the next quarter.

Task 2 - Plug Flow Combustor Tests

Task 2 work planned for the following quarter includes a final check out of the plug flow combustor. Testing at the plug flow facility is currently scheduled to begin early in CY 1990.

Task 3 - Coal Selection

It is expected that the two coals required for Task 4 testing will be selected during this time. The coals will then be prepared and delivered to the coal-combustor facility at UCI.

Task 4 - Coal-Fired Combustor Tests

It is anticipated that preparation of the combustor for the coal tests will be completed during this quarter. Following this, the Task 4 work will include the testing on the coal-fired combustor.

Task 5 - Data Analysis and Reporting

It is anticipated tha data analysis activities will pick up during this quarter, provided that laboratory test data become available. Preparation of monthly and quarterly progress reports will continue.

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