UC Irvine

UC Irvine Previously Published Works

Title

Formation and measurement of N₂O in combustion systems

Permalink

<https://escholarship.org/uc/item/0ph713f1>

Journal

Symposium (International) on Combustion, 23(1)

ISSN

0082-0784

Authors

Muzio, LJ
Montgomery, TA
Samuelsen, GS
[et al.](#)

Publication Date

1991

DOI

10.1016/S0082-0784(06)80266-3

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed

FORMATION AND MEASUREMENT OF N_2O IN COMBUSTION SYSTEMS

L. J. MUZIO, T. A. MONTGOMERY

Fossil Energy Research Corporation

G. S. SAMUELSEN

University of California, Irvine

J. C. KRAMLICH, R. K. LYON

Energy and Environmental Research Corporation

AND

A. KOKKINOS

Electric Power Research Institute

Direct N_2O emissions from fossil fuel combustion have previously been reported to be equivalent to 25–40% of the NO_x levels. At these levels, fossil fuels have been suggested to be a major anthropogenic source of N_2O . Recent tests have shown these measurements to be in error, most of the N_2O having been formed by reaction between NO_x , SO_2 , and H_2O in the sample containers. Time resolved measurements of gas samples stored in Tedlar bags, supported by chemical kinetic calculations, indicate that the majority of N_2O forms over a time period of 6 hours. The conversion of NO_x to N_2O in the sample containers is shown to depend on the amount of SO_2 present.

This sampling artifact raises questions about the validity of the existing data base, collected by grab sampling methods. As a result, a continuous infrared analyzer, developed primarily for characterization of N_2O emissions from full scale combustion sources, was used to perform on line N_2O measurements at several full scale utility combustion systems. A variety of conventional and advanced utility combustion systems (firing pulverized coal, oil, and gas) were tested. The measurements from conventional systems (natural gas, oil, and pulverized coal-fired) indicate that the direct N_2O emission levels are generally less than 5 ppm and are not related to the NO_x levels in the flue gas. However circulating fluidized bed units produced elevated N_2O emissions. At one circulating fluidized bed combustor firing a bituminous coal, N_2O levels ranged from 84 to 126 ppm as the load was varied from 100% to 55%, respectively. The N_2O emissions from the circulating fluidized bed appeared to be inversely related to the bed temperature. However, temperature is not the only parameter affecting N_2O emissions from fluidized beds; all three of the units studied operated at similar temperatures during full load operation, but the N_2O emissions ranged between 25 and 84 ppm. N_2O emissions were also elevated at a full-scale boiler using selective non-catalytic NO_x reduction with urea; 11–13% of the reduced NO_x was converted to N_2O .

Background

The mean global concentration of N_2O is approximately 300 ppb and has been increasing at a rate of 0.2–0.4% per year.^{1,2} In the troposphere, N_2O is a relatively strong absorber of infrared radiation, and, therefore implicated as a contributor to the "Greenhouse Effect." Being stable in the troposphere, N_2O is transported to the strato-

sphere. In the stratosphere N_2O is the largest source of stratospheric NO ; NO is the primary species responsible for establishing the equilibrium stratospheric O_3 concentration.³

The increase of N_2O in the atmosphere has been attributed to anthropogenic sources, although the dominant source of N_2O is still uncertain. Weiss,² Hao et al.,⁴ and Tirpak¹ suggest that combustion of fossil fuels results in emissions of N_2O that can ac-

count for the observed increase in N₂O. Previous N₂O measurements from combustion sources indicate that systems fired with natural gas do not produce significant concentrations of N₂O. However, substantial levels of N₂O were reported from systems fired with residual oil or coals (e.g., fuels containing nitrogen and sulfur). In fact, the measurements of Hao et al.⁴ and Castaldini et al.⁵ suggest that the N₂O emissions are related to the emissions of NO_x (NO + NO₂); the N₂O level being equal to 25–40% of the NO_x concentration.

The N₂O measurements from combustion sources referenced above were made 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 the containers creating N₂O concentrations substantially higher than those originally formed in the combustion process.^{6,7} This raises questions regarding the existing data base on N₂O emissions from combustion sources and the role of combustion in contributing to the increases in atmospheric N₂O concentration.

This paper will address two issues: 1) the formation of N₂O in sample containers; and 2) N₂O emissions from combustion systems using an on-line continuous infrared analyzer.

Formation of N₂O in Sample Containers

The artifact in measuring N₂O with grab sampling techniques was initially identified in the course of combustion experiments in a bench-scale combustor.^{6,7} The tests showed that the N₂O was being formed in the sample containers through a reaction mechanism involving SO₂, NO, and H₂O.^{6,7} The SO₂ concentration was found to influence the amount of N₂O formed. To better quantify the progress of the reactions occurring in the sample containers, tests were conducted during this study to determine the time history of N₂O, NO, NO₂, and SO₂ in the sample containers. Gas samples from a natural gas fired combustor were collected in 270 liter Tedlar bags and subsequently analyzed for NO, NO₂, N₂O and SO₂. The 270 liter Tedlar bags provided sufficient sample to allow samples to be withdrawn and analyzed as a function of time using continuous gas analyzers. N₂O was analyzed with an infrared continuous analyzer described in Ref. 8. NO and NO_x were measured with a TECO chemiluminescent analyzer and SO₂ with a Western Research ultraviolet analyzer.

The primary variable for the series of tests was SO₂ concentration, which was varied from 700 ppm to 2500 ppm. Initial SO₂ and NO_x concentrations were varied by adding SO₂ to the combustion air and NH₃ to the natural gas. The time histories of N₂O, NO_x, and SO₂ are shown in Fig. 1. As can

FIG. 1. Time histories of N₂O, NO_x, and SO₂ during reaction in 270 liter Tedlar bags: experimental versus model results: a. N₂O, b. NO_x, c. SO₂ (— experimental, --- model).

be seen in Fig. 1a, the majority of the N₂O formation occurs in the first six hours, irrespective of the initial SO₂ level. The accompanying time histories of NO_x and SO₂ are shown in Figs. 1b and 1c. As seen in Figs. 1a–c, at the high SO₂ condition, virtually all of the NO_x initially present in the

Tedlar bag is transformed to N₂O in the final product. At the lowest SO₂ concentration (716 ppm), N₂O continues to form until virtually all of the SO₂ is removed from the gas phase, after which the N₂O stabilizes while the NO_x continues to decrease. At the intermediate SO₂ level (1210 ppm), the N₂O formation rate is initially rapid becoming more gradual after 2 hours, as the NO_x and SO₂ are consumed. For this intermediate case, there appears to be sufficient SO₂ to allow the reaction to proceed longer than at the low SO₂ condition, but not sufficient SO₂ to convert all of the initial NO_x to N₂O, as was observed at the higher SO₂ level.

The gas phase and aqueous reactions between SO₂, NO_x, and H₂O leading to the formation of N₂O have been documented in the literature. Martin et al.⁹ discuss the reaction mechanism; the general chemistry has also been discussed in the wet FGD scrubbing literature.^{10,11} Lyon and Cole¹² proposed a detailed mechanism for N₂O formation in the sample containers. In the sample flasks, NO is oxidized to NO₂. NO₂ and SO₂ in the gas phase are taken to be in equilibrium with the aqueous phase. In the aqueous phase, the NO₂ and SO₂ ultimately form N₂O and H₂SO₄ through a reaction sequence involving HNO.¹²

The detailed mechanism of Lyon and Cole was integrated for the same conditions as the experiments conducted in the Tedlar bags (Fig. 1). The results of these calculations are included with the experimental results in Figure 1a–c. In general, the model calculations are in qualitative agreement with the experimental results. The characteristic time for N₂O formation is basically the same between experiment and model, with the experiment exhibiting somewhat faster N₂O formation than predicted by the model. However, there are noteworthy differences between the experiments and the model calculations. First, for the medium and high SO₂ cases, the kinetics underpredict the amount of N₂O formed. At the high SO₂ condition, the experiments exhibited virtually 100% conversion of the NO_x to N₂O, whereas the model predicts 65% conversion. Second, in the Tedlar bags the rate of disappearance of NO_x decreased as the SO₂ level decreased, whereas the kinetic calculations indicate little effect of SO₂ level upon the NO_x time histories. Another difference between the experimental observations and calculations is the effect of the chemical reactions on the pH of the aqueous phase. Experimentally, the pH in sample containers containing 600 ppm NO and 1500 ppm of SO₂ have been reported to be 1.8.⁷ However, the calculations indicate an aqueous phase pH of only 4.5–4.8 after 24 hours for initial SO₂ concentrations ranging from 2470 ppm to 100 ppm. This is expected to influence the calculated levels of N₂O produced since previous work suggests that N₂O increases as the pH decreases.^{10,11}

At present, the model does not include a reaction allowing the direct oxidation of sulfite ion to sulfate ion, although this step is known to occur. By including this reaction in the model, most of the deviations noted in Fig. 1 could be accounted for. For example, the sulfite ion concentration would be depleted, reducing the resistance of the liquid phase to SO₂ dissolution. This would increase the predicted rate of SO₂ decay in the gas phase, improving agreement between model and experiment (Fig. 1). Also, the depleted sulfite ion in the liquid phase would slow the liquid phase conversion of nitrogen, thereby increasing the resistance of NO₂ entering the liquid phase. Finally, the missing reaction would accelerate the conversion of a weak acid into a strong acid, reducing the predicted pH toward the experimentally observed values of 1.7–1.9.

N₂O Emissions from Combustion Sources

Reliable measurements of N₂O emissions from combustion systems are needed in order to assess the role of combustion as an anthropogenic source of atmospheric N₂O. With grab sampling procedures in question, a continuous N₂O analyzer, utilizing a non-dispersive infrared principle was used to characterize N₂O emissions from a variety of utility scale combustion systems. The continuous N₂O analyzer system is described in detail elsewhere.⁸ The basic analyzer is a non-dispersive infrared analyzer manufactured by Horiba Ltd. based on the work by Montgomery, et al.⁸ The analyzer utilizes a 500 mm sample cell and uses the 7.8–8.5 micron region of the infrared for the N₂O measurement. To eliminate interferences, NO₂ and SO₂ are removed from the sample gas using 1 M solutions of sodium sulfite and sodium carbonate.⁸

The continuous N₂O analyzer was used to characterize the N₂O emissions from the following systems:

Natural Gas-Fired Utility Boilers	(3 units)
Residual Oil-Fired Utility Boilers	(2 units)
Pulverized Coal-Fired Utility Boilers	(7 units)
Circulating Fluidized Bed Combustors	(3 units)
Boiler with Selective Non-Catalytic	
NO _x Reduction	(1 unit)

The units firing natural gas, oil, and pulverized coal comprised a variety of designs including single wall-fired, opposed wall-fired and tangentially fired, and ranged in size from 50 to 750 MW (electric). The majority of the testing was performed at full load. For selected sites, the testing was performed over a range of loads. A summary of the results is pre-

sented in Table I. At four of the boilers, on-line gas chromatographic measurements sponsored by the U.S. EPA were made in parallel and showed similar results.¹³

Natural Gas Firing:

The N₂O emission from three natural gas-fired utility boilers ranging in size from 215 to 750 MW were consistent with the previously reported results.² The N₂O emissions from these natural gas-fired utility boilers were low, less than 2 ppm. Also, as seen in Table I, there was no correlation with the NO_x emissions.

Residual Oil Firing:

The N₂O emissions from the two residual oil-fired utility boilers (110 and 215 MW) were again low, 1 ppm, and exhibited no correlation with the NO_x emissions.

Pulverized Coal Firing:

Seven pulverized coal-fired boilers were tested ranging in size from 180 MW to 790 MW. As can be seen in Table I, except for the 620 MW opposed wall-fired boiler, the N₂O emissions were less than 6 ppm. The 12 ppm N₂O concentration measured from the 620 MW opposed-fired unit may represent an upper limit on the emissions from this unit. Because of the high SO₂ levels and NO_x levels in this flue gas, a small amount of N₂O may have formed in the unheated sample lines during transport to the analyzer.

Circulating Fluidized Bed Combustion:

N₂O emissions were also characterized at three circulating fluidized bed combustors. Compared to pulverized coal-fired boilers, the circulating bed units exhibit elevated levels of N₂O emissions. At full load operation of these units, N₂O levels ranged from 84 to 26 ppm (dry at 3% O₂).¹⁴ The corresponding NO_x levels varied from 81 to 283 ppm (dry at 3% O₂).¹³ At one of the units, tests were conducted over a range of operating loads, from 55 to 100% of rated load. A summary of this unit's emissions are presented in Table II. The N₂O and NO_x levels are plotted as a function of load in Figure 2a. For this unit, the N₂O levels decrease and NO_x increases as the load increases. Further, for this unit the N₂O and NO_x emissions appear to correlate with bed temperature (see Fig. 2b). The N₂O levels decrease and NO_x increases as the bed temperature increases. The trends in N₂O concentrations with bed temperature are consistent with the results obtained from pilot-scale fluidized bed combustors reported by Amand and Anderson¹⁵ and the mechanism suggested by Kramlich et al.¹⁶ Kramlich et al.¹⁶ suggest that N₂O formation can occur from HCN through a mechanism of the form

Peak conversion of HCN to N₂O via the above

TABLE I
N₂O emissions from full-scale utility combustion systems

Design Type	Fuel	Load (%)	NO _x * (ppm)	N ₂ O* (ppm)
Single Wall-Fired Boiler	Nat. Gas	98	120	2
Opposed-Fired Boiler	Nat. Gas	97	142	2
T-Fired Boiler	Nat. Gas	100	58	1
Single Wall-Fired Boiler	Resid. Oil	100	268	1
Single Wall-Fired Boiler	Resid. Oil	91	291	2
Opposed-Fired Boiler	Pulv. Coal	97	982	12
Opposed-Fired Boiler	Pulv. Coal	97	701	3
Opposed-Fired Boiler, Triple Cell	Pulv. Coal	98	692	6
T-Fired Boiler	Pulv. Coal	95	325	1
T-Fired Boiler	Pulv. Coal	82	390	1
T-Fired Boiler	Pulv. Coal	69	393	1
T-Fired Boiler	Pulv. Coal	51	498	1
Circulating Fluidized Bed	Crushed Coal	100	81	84

*Corrected to 3% O₂.

TABLE II
Emissions from the circulating fluidized bed combustor

Load % of Rated	T _{bed} °K	O ₂ % dry	CO ₂ % dry	CO ppm dry	SO ₂ ppm corrected to 3%	NO O ₂ dry	N ₂ O O ₂ dry
55	1116	5.0	14.6	127	86	55	126
75	1141	3.9	15.6	76	79	61	93
100	1146	3.6	16.0	86	81	81	84

mechanism occurs at a temperature of about 1250 K. Below 1250 K, N₂O concentrations are controlled by the formation of NCO and the conversion of NCO to N₂O. Above 1250 K, removal of N₂O through reactions with H and OH control the level of N₂O. At the circulating fluidized bed tested over a range of loads, bed temperatures ranged between 1116 and 1140 K, suggesting that the N₂O levels from this unit are controlled by formation processes rather than destruction reactions.

Further investigations are needed to assess what other operational variables yield higher or lower N₂O levels in CFBC's. While N₂O levels correlated with bed temperature for the unit where tests were conducted over a range of loads, all three of the units tested operated at similar bed temperatures at full load. Yet, the N₂O levels varied from 26 to 84 ppm. Other parameters that might influence the level besides temperature include the fuel type (char N evolution), char and/or solids loading, residence time, calcium species, sulfur species, and NO_x level. Certainly the field data suggest there are operational conditions that minimize N₂O in CFBC's, offering possible keys to its control. Once the primary N₂O formation mechanisms are understood, potential control mechanisms can be developed.

FIG. 2. N₂O and NO_x emissions versus load from a circulating fluidized bed combustor. (a. as a function of load; b. as a function of bed temperature).

Selective Non-Catalytic NO_x Reduction: Urea Injection

A number of selective non-catalytic NO_x reduction processes (SNCR) are currently under development for utilization in industry. These include injection of ammonia (NH₃), urea (NH₂CONH₂), or cyanuric acid ([HNCO]₃) at temperatures nominally between 1200 and 1500 K where the decomposition products react with NO_x. Caton and Siebers¹⁷ reported bench-scale results showing N₂O as a product of the reaction between cyanuric acid and NO_x, presumably via reactions 3 and 4. Further, they suggested that urea injected into high temperature combustion products would decompose to NH₃ and HNCO.

N₂O measurements were also made at a unit using urea injection to reduce NO_x. The boiler is rated at 110 MW and was firing residual oil. A summary of the full load data is presented in Table III. The urea/NO_x molar injection ratio was varied between 0.0 (baseline) and 0.6. Without urea injection, the baseline NO_x and N₂O emissions were 291 and 1 ppm, respectively. As the amount of urea injection increased, the NO_x level decreased, and the N₂O level increased. Over the range of urea injection rates tested (urea/NO_x molar ratio of 0.2 to 0.6), between 11 and 13% of the NO_x removed was converted to N₂O. Further work is needed to 1) verify these first measurements, 2) thoroughly characterize N₂O formation from SNCR processes, and 3) develop a better understanding of the basic N₂O formation chemistry.

TABLE III
N₂O and NO_x emissions: oil-fired boiler with urea injection

Urea/NO _x (molar ratio)	NO _x (ppm)	N ₂ O (ppm)	ΔNO _x (%)	ΔN ₂ O ΔNO _x
0.0	291	1	—	—
0.2	206	10	29%	11%
0.4	161	16	45%	12%
0.6	117	23	60%	13%

Conclusions

The following conclusions can be drawn from the results discussed above:

- N₂O measurements using grab sampling techniques are subject to errors due to reactions between NO, SO₂, and H₂O forming N₂O in the sample containers. The N₂O formation occurs over a time period of 2–6 hours and depends on the amount of SO₂ initially present.
- Measurements using the continuous analyzer at a variety of conventional utility boilers (natural gas, residual oil, and pulverized coal-fired) indicate that direct N₂O emissions are low (generally, less than 6 ppm), and that the N₂O levels are not a substantial fraction of the NO_x levels as previously suggested.
- Tests of circulating fluidized bed combustors yielded N₂O levels ranging from 26 to 84 ppm. The N₂O levels appear to be inversely related to the fluidized bed temperature.
- N₂O measurements at a full-scale boiler using urea injection for NO_x reduction show that 11–13% of the reduced NO_x is converted to N₂O.
- Further work is needed to determine if the chemistry occurring in the sample containers plays a role in increasing atmospheric N₂O concentrations; e.g., if NO_x, SO₂, and H₂O react in the atmosphere to form N₂O.

Acknowledgments

We are pleased to acknowledge the support of the Electric Power Research Institute at Fossil Energy Research Corp. (Contract No. RP2533-9), and at the University of California, Irvine (Contract No. RP8005-4) in the development of the continuous N₂O analyzer. The field measurements made with the continuous analyzer were supported by the Electric Power Research Institute and Southern California Edison (Contract No. RP2154-16). Additionally, we are pleased to acknowledge the support of the U.S. Department of Energy's Direct Utilization Advanced Research and Technology Development Program at Energy and Environmental Research (Contract No. DE-AC22-84PC70771) in the chemical kinetic modeling of N₂O formation in sample containers. We would like to acknowledge and thank HORIBA, Ltd. for their cooperation and support in the development of the field prototype N₂O analyzer. The continued encouragement and discussions with G. Offen (EPRI) and Kert Kertamus (SCE) are also acknowledged. K. Anderson, M. Teague, G. Shiimoto, J. A. Cole, T. Grogan, J. M. Mc-

Carthy, T. McGrath, and J. McInerney helped in the performance of the experimental tasks and modeling.

REFERENCES

1. TIRPAK, D. A.: Symposium on Stationary Combustion Nitrogen Oxide Control, V. 1, EPRI CS-5361, EPA Contract 68-02-3994, WA93, 1987.
2. WEISS, R. F.: *J. Geophys. Res. Lett.*, 86 (C8), 7285 (1981).
3. KRAMLICH, J. C., LYON, R. K., AND LANIER, W. S.: EPA/NOAA/NASA/USDA N₂O Workshop, Volume I: Measurement Studies and Combustion Sources, EPA-600/8-88-079, 1988.
4. HAO, W. M., WOFSY, S. C., MCELROY, M. W., BEER, J. M., AND TOQUAN, M. A.: *J. Geophys. Res.*, 15, 1369 (1987).
5. CASTALDINI, C., et al.: 1982 Joint Symposium on Stationary Combustion NO_x Control, V. II, 46.1-46.24, EPA-600/9-85-0266, U.S. Environmental Protection Agency, 1983.
6. MUZIO, L. J. AND KRAMLICH, J. C.: *Geophys. Res. Lett.*, 15, 1369 (1988).
7. MUZIO, L. J. et al.: *JAPCA*, 39, 287 (1989).
8. MONTGOMERY, T. A., MUZIO, L. J., AND SAMUELSEN, G. S.: *JAPCA*, 39, 721 (1989).
9. MARTIN, L. R. et al.: *Atmos. Environ.*, 15, 191 (1981).
10. CHANG, A. G. et al.: in *Flue Gas Desulfurization*, (J. L. Hudson and G. T. Rochelle, Eds.) ACS Symposium Series 188, p. 127, American Chemical Society, Washington, D.C., 1982.
11. NARITA, E. et al.: *Ind. Eng. Chem. Prod. Res. Dev.*, 23, 262 (1984).
12. LYON, R. K. AND COLE, J. A.: *Comb. Flame*, 77, 139, 1988.
13. CLAYTON, R. et al.: N₂O Field Study, EPA-600/2-89-006, U.S. Environmental Protection Agency, 1989.
14. MONTGOMERY, T. A., et al.: N₂O Emissions from Full Scale Combustion Systems, to be submitted to *JAPCA*, 1990.
15. AMAND, L. E., AND ANDERSON, S.: Emissions of Nitrous Oxide (N₂O) from Fluidized Bed Boilers, presented at the Tenth International Conference on Fluidized Bed Combustion, San Francisco, California, 1989.
16. KRAMLICH, J. C., COLE, J. A., MCCARTHY, J. M., LANIER, W. S., AND MCSORLEY, J. A.: *Comb. Flame*, 77, 375 (1989).
17. SIEBERS, D. C., AND CATON, J. A.: *Comb. Sci. Tech.*, 65, 277 (1989).