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Project Summary

Environmental Assessment of NH_3 Injection for an Industrial Package Boiler

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This report discusses emission results from comprehensive flue gas sampling of a gas- and oil-fired industrial boiler equipped with Exxon's Thermal DeNO$_x$ Ammonia Injection Process for NO$_x$ reduction. The objective of the tests was to evaluate criteria and noncriteria pollutant emissions in the flue gas during a baseline (uncontrolled) and a low-NO$_x$ condition with ammonia injection. The test boiler was a 7.57 kg/s (60,000 lb/hr) watertube unit equipped with sidefire air and Thermal DeNO$_x$. Comprehensive emission measurements included continuous monitoring of flue gas emissions; source assessment sampling system (SASS) testing with subsequent laboratory analysis of samples to give total flue gas organics in two boiling point ranges, specific quantitation of semivolatile organic priority pollutant species, and flue gas concentrations of 73 trace elements; EPA Method 5/17 for solid and condensible particulate emissions and ammonia emissions; controlled condensation system for SO_2 and SO_3; and N_2O emission sampling.

Comparison of the baseline and controlled emission results showed that ammonia injection at a NH_3/NO molar ratio of 2.52 gave a NO$_x$ reduction of 41 percent from an uncontrolled level of 234 ppm to a controlled level of 137 ppm (corrected to 3 percent O_2). NH_3 emissions increased from 11 ppm for the baseline to an average of 430 ppm for ammonia injection. Nitrous oxides, N_2O, was reduced 68 percent from a 50 ppm baseline level to a 17 ppm controlled level. Total particulate emissions increased by an order of magnitude from a baseline of 17.7 ng/J (0.042 lb/10^6 Btu) to a controlled level of 182 ng/J (0.43 lb/10^6 Btu). This increase is in part attributed to formation of ammonia sulfate and bisulfate from residual ammonia and SO$_x$. Total organic emissions were at a moderate level and showed a relative concentration in the nonvolatile category (boiling point greater than 300 °C). Organic emissions were lower by a factor of five with ammonia injection. Emissions of carbon monoxide and trace inorganic elements were not significantly affected by ammonia injection.

This Project Summary was developed by EPA's Air and Energy Engineering Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in two separate volumes (see Project Report ordering information at back).

Introduction

Increasing stringency in stationary source NO$_x$ emissions regulations has created applications for advanced control technologies. Over the past 5 years, the Exxon Thermal DeNO$_x$ selective noncatalytic reduction process has been installed in a number of process heaters and boilers to augment NO$_x$ reduction from combustion modification at a lower cost than selective catalytic reduction. This process reduces NO$_x$ through the gas-phase reaction with ammonia in the temperature range of 870 to 1,200 °C (1,600 to 2,200 °F). NO$_x$ reduction as high as 60 to 70 percent has been achieved in some industrial applications. The reduction efficiency is affected by the NH_3 feed rate relative to NO$_x$ concentrations, by the degree of flue gas thermal stratification in the ammonia injection section, and by the flue gas residence time within the appropriate temperature window. Potential emission side-effects of the process include the presence of unreacted ammonia in the flue gas and the formation of ammonium sulfates for sources fired with sulfur bearing fuels. Few data have been reported on the effects of full-scale ammonia injection on emissions of other inorganic and organic species. This test was undertaken to perform a comprehensive emission characterization of the boiler with and without ammonia injection to supply data on overall emission impacts of the process. This test was conducted as part of the Combustion Modification Environmental Assessment Program under which similar tests have been performed on 17 boilers, process heaters, and engines.

Summary and Conclusions

Source Description

The boiler tested was a packaged two-drum Zurn Keystone watertube unit equipped with an economizer and a rated capacity of 7.57 kg/s (60,000 lb/hr) of superheated steam at 2.51 MPa (350 psi) and 260 °C (500 °F). The boiler was equipped with a single ammonia injection grid to mix ammonia with the combustion gases in the appropriate temperature window. Steam was used as the ammonia carrier. Hydrogen injection with the ammonia was also available to lower the effective temperature range for use at low load operation.

Test Program

Two tests were performed: a baseline uncontrolled run, and an ammonia injection controlled run. Boiler steam flowrate was about 4.0 kg/s (32,000 lb/hr) for both tests, corresponding to a total steam input of about 13 MW (45 million Btu/hr). The boiler was fired with refinery gas and residual oil. Refinery gas supplied 44 percent of the total heat input. Ammonia injection rates for the controlled test were 1.53 g/s (12.1 lb/hr) corresponding to a NH_3/NO molar ratio of 2.5.

The program for emission measurements at the two test conditions conformed to a modified EPA level 1 protocol. In addition, NH_3 flue gas emissions were measured to calculate the amount of unreacted NH_3 being emitted under the boiler and control system parameters investigated. Flue gas was measured at the stack downstream of the boiler economizer where the gas temperature was about 188 °C (370 °F). Flue gas measurements included:

- Continuous monitors for NO_x, CO, CO_2, and O_2.
- Source assessment sampling system (SASS) train sampling for organic and inorganic pollutant species.
- EPA Method 5 with water impingers and an EPA Method 17 backup for solid and condensible particulate mass emissions.
- Controlled condensation system (CCS) for SO_2 and SO_3
- Grab sample for onsite analysis of gaseous C_1 to C_6 hydrocarbons by gas chromatography.
- EPA Method 17 with HCl impinger solutions for ammonia sampling.

In addition to this detailed test program, short-term tests (varying NH_3/NO molar ratio, hydrogren injection, and oil/gas fuel ratio) were performed. The objective of these short-term tests was to map the performance of the Thermal DeNO_x Process over a wide range of system and boiler operating parameters. Measurements for these short-term tests were confined to continuous monitoring of O_2 and NO_x.

Emission Measurements and Results

Results of the short-term performance tests are summarized in Figure 1. Baseline NO_x emissions averaged 235 ppm at 3 percent O_2 for two oil/gas fuel mixtures investigated. The results show that NO_x reduction for a given NH_3/NO ratio depends on the fuel mixture. The system was less effective at the oil/gas ratio of 56/44 percent than at the lower oil/gas ratio of 37/63 percent (closer to the typical operation of the unit and the design basis for the NH_3 injection grid installed). The addition of hydrogen did not improve system performance at the lower oil/gas ratio, but resulted in significant, further NO_x reduction to levels below 100 ppm at the higher oil/gas ratio. With the higher oil/gas ratio, boiler convective section gas temperatures are lower at the grid location, thereby decreasing the effectiveness of NH_3 alone.

For both fuel mixtures, the NO_x reduction performance appears to peak at a NH_3/NO ratio of about 2.5 with little or no additional reduction gained with further increase in NH_3 injection rate.

Table 1 summarizes criteria and other gas species emissions measured during the two comprehensive tests. NH_3 injection, at a rate of 2.52, resulted in a 41 percent NO_x reduction. CO emissions showed no significant change. Indications of higher

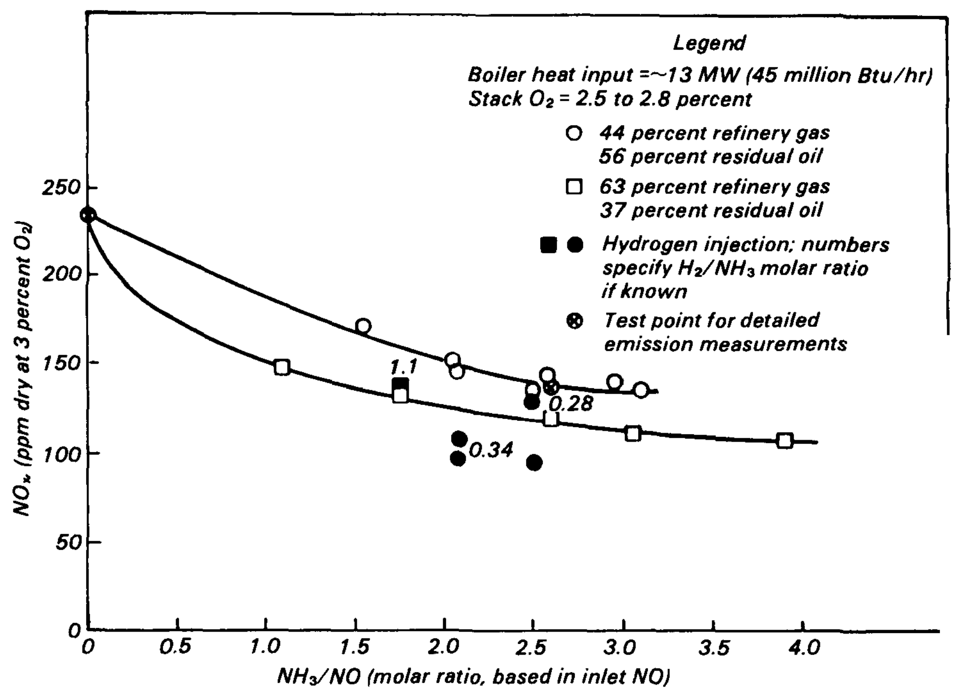

Figure 1. *Thermal De NO_x performance on the packaged industrial boiler.*

Table 1. Criteria and Other Gas Species Emissions

Pollutant	Test 1 (baseline)			Test 2 (NH_3 injection)		
As measured by:						
Continuous gas analyses						
O_2, percent	2.6			2.5		
CO_2, percent	11.7			11.6		
NO_x, ppm	239			141		
CO, ppm	31			24		
Wet chemical methods						
SO_2, ppm	NA			82		
SO_3, ppm	NA			13		
NH_3, ppm	11[a]			440[b]		
Offsite gas chromatography						
N_2O	53			17		
Onsite gas chromatography						
C_1, ppm	ND			0.8		
C_2, ppm	ND			0.6		
C_3, ppm	2.6			ND		
C_4, ppm	ND			6.2		
C_5, ppm	ND			5.1		
C_6, ppm	ND			5.0		
Corrected emissions	ppm[c]	ng/J[d]	lb/10^6 Btu[d]	ppm	ng/J	lb/10^6 Btu
NO_x[e]	234	115	0.268	137	67	0.16
CO	30	9.0	0.02	23	6.9	0.02
SO_2	NA	NA	NA	80	55	0.13
SO_3[f]	NA	NA	NA	13	13	0.03
NH_3[g]	11	2.0	0.005	430	78	0.18
N_2O	52	25	0.056	17	8.0	0.019
C_1	—	—	—	0.8	0.15	0.0003
C_2	—	—	—	0.6	0.21	0.0005
C_3	2.5	1.3	0.003	—	—	—
C_4	—	—	—	6.0	3.2	0.007
C_5	—	—	—	5.0	4.3	0.010
C_6	—	—	—	4.9	5.0	0.012
Total C_1 to C_6	2.5	1.3	0.003	17.0	13.0	0.030
Particulate mass Emissions:						
Method 5/17 solid	—	4.6	0.01	—	1.8	0.004
Method 5/17 condensible inorganic	—	10.0	0.023	—	180	0.42
Method 5/17 condensible organic	—	2.9	0.007	—	0.2	0.0004
Method 5/17 total	—	17.7	0.042	—	182	0.43
SASS solid	—	2.2	0.005	—	2.6	0.006

[a]NH_3 emissions ranged from 3 to 25 ppm from three separate flue gas measurements
[b]NH_3 emissions ranged from 280 to 600 ppm from two separate flue gas measurements
[c]Dry ppm at 3 percent O_2
[d]On heat input basis
[e]As NO_2
[f]As H_2SO_4
[g]Arithmetic average
NA — Sample lost in transit
ND — Not detected

gaseous hydrocarbons, especially in the C_4 to C_6 range, were recorded with ammonia injection. This may have been due to burner tip coking which required frequent cleaning.

Baseline NH_3 emissions ranged from 3 to 25 ppm, averaging 11 ppm (0.23 lb/hr). During NH_3 injection, unreacted NH_3 emissions from two consecutive measurements ranged between 200 and 600 ppm, averaging 430 ppm (8.4 lb/hr). A third measurement resulted in NH_3 concentrations of 840 ppm (16.0 lb/hr). This measurement was considered erroneous because it resulted in more NH_3 emitted than actually injected through the grid. Analyses of the EPA Method 5 and 17 impinger solutions indicated concentrations of NH_3 corresponding to a stack concentration of about 6 ppm (0.12 lb/hr) for baseline and 360 ppm (7 lb/hr) for the NH_3 injection test. These results are in general agreement with the ammonia emission sampling system.

Nitrous oxide (N_2O) averaged about 50 ppm during baseline, and dropped to 17 ppm during the second test. This 68 percent reduction in N_2O exceeds the 41 percent reduction in NO_x.

Total particulate matter during the NH_3 injection test increased by more than one order of magnitude. The largest contribution to this increase was from the inorganic condensate matter collected in the impinger section. This can be in part explained by ammonium sulfate and bisulfate formed either in the stack or through the particulate sampling system.

SASS samples were analyzed for organic content and inorganic trace elements. Total chromatographable organics, hydrocarbons in the boiling range of 100° to 300°C (210 to 570°F), measured 0.023 ng/J (90 μg/dscm) for the baseline and 0.01 ng/J (40 μg/dscm) for the NH_3 injection test. Organics measured by gravimetry (GRAV) analysis for hydrocarbons having boiling points greater than 300°C (>570°F) were 0.29 ng/J (1,300 μg/dscm) for the baseline and 0.059 ng/J (240 μg/dscm) for the NH_3 injection test. Infrared spectra of the gravimetric residue suggest the presence of aliphatic hydrocarbons and alcohols for both tests.

The XAD-2 extract of the baseline test, which contained the highest organic content, was also subjected to liquid chromatography separation. There were no discernable peaks from fractions 2 through 4. These spectra indicate that, of the 1.2 mg/dscm of organic matter in the total sample, about 70 percent is aliphatic hydrocarbons, 20 percent is alcohols, and 10 percent is carboxylic acids.

Gas chromatography/mass spectrometry analysis of sample extracts was performed to determine the presence and concentration of 58 semivolatile organic priority pollutants. Of these, the only ones detected were naphthalene, phenanthrene, and phenol in amounts corresponding to flue gas concentrations generally <1 μg/dscm.

Results of spark source mass spectrometry (SSMS) and atomic absorption spectrometry (AAS) indicated that inorganic trace elements were not affected by NH_3 injection. Major elements having flue-gas concentrations exceeding 50 mg/dscm for both tests included: sulfur, copper, nickel, silicon, titanium, vanadium, zinc, potassium, cobalt, fluorine, and iron. These emissions are most likely the result of:

- Inorganic elements in the fuel oil.
- Erosion of metal surfaces by the hot combustion gases in the boiler passes, including the NH_3 injection grid.
- Erosion of sampling equipment metal parts.

Summary

Emissions from an industrial boiler firing refinery gas and residual oil were tested with and without the Thermal DeNO$_x$ ammonia injection process. NO$_x$ reductions of 30 to 60 percent were observed depending on the ammonia injection rate, the relative amount of gas and oil fired, and the use of hydrogen injection with the ammonia. The primary emission effect on other species was the formation of ammonium sulfate and the discharge of unreacted ammonia.

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The complete report consists of two volumes, entitled "Environmental Assessment of NH_3 Injection for an Industrial Package Boiler."

"Volume I. Technical Results," (Order No. PB 86-159 852/AS; Cost: $16.95)

"Volume II. Data Supplement," (Order No. PB 86-182 409/AS; Cost: $22.95)

The above documents will be available only from: (cost subject to change)

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