United States
Environmental Protection
Agency

Industrial Environmental
Research Laboratory
Research Triangle Park NC 27711

Research and Development

EPA-600/S7-84-074 Sept. 1984

Project Summary

Environmental Assessment of a Crude-Oil Heater Using Staged Air Lances for NO_x Reduction

R. DeRosier

This report describes emission results obtained from field tests of a crude-oil process heater burning a combination of oil and refinery gas. The heater had been modified by adding a system for injecting secondary air to reduce NO_x emissions. One test was conducted with the staged air system (low-NO_x), and the other, without (baseline). Tests included continuous monitoring of flue gas emissions and source assessment sampling system (SASS) sampling of the flue gas with subsequent laboratory analysis of samples utilizing gas chromatography (GC), infrared spectrometry (IR), gas chromatography/mass spectrometry (GC/MS), and low resolution mass spectrometry (LRMS) for organics. Atomic absorption spectrometry (AAS) and spark source mass spectrometry (SSMS) were used for trace metal analysis. Flue gas concentrations of NO_x were reduced 30 percent (from 83 to 56 ng/J) with the staged air system. Total organic emissions dropped from 17.1 to 3.4 mg/dscm from the baseline to the low-NO_x test, due primarily to a reduction in the C_1 to C_6 boiling point range compounds which constituted most of the organic emissions. GC/MS analysis identified 11 semivolatile priority pollutant compounds in both tests, most of them present in higher concentrations during the baseline test. LRMS analysis suggested the presence of eight compound categories in the organic emissions during the baseline test and four compound categories in the low-NO_x test. Radiometric analysis of the flyash particulate indicated no measurable radionuclide emissions. Biological tests indicated that the sorbent module extracts from both tests were of moderate toxicity and moderate-to-high mutagenicity.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Advanced forms of combustion modifications have been developed in recent years as a way to reduce NO_x emissions without adverse consequences, such as capacity loss caused by derating the unit. Staged combustion using air injection lances is one form of combustion modification that is relatively easy to retrofit to industrial-sized combustion equipment since it requires relatively minor hardware modification. The report describes the results of testing a refinery crude-oil heater fitted with air injection lances. The unit was tested with and without the staged combustion system in operation. The flue gas was analyzed for criteria pollutants as well as noncriteria organic and inorganic species.

The crude-oil process heater tested has a rated maximum firing rate of 16-MW (55 million Btu/hr) heat input. The heater uses six John Zink DBA-22 natural-draft burners that can fire a combination of oil and gas. The heater had been modified by adding a system to inject secondary air to reduce NO_x emissions. This system consists of a fan to supply the air, a manifold and associated tubing, and 24 (4 per burner) variable-height air lances. The air lances can deliver half of the stoichiometric combustion air; the rest of the combustion air is delivered through secondary air registers at the base of the heater. Air flow through the heater is controlled by a damper above the convection section.

Summary

Heater Operation

The test plan called for exhaust gas emission measurements under both baseline and low-NO_x operation. Table 1 summarizes the heater operating conditions for each test. Originally the tests were to be conducted while firing a 50/50 mixture (by heat input) of oil and refinery gas. However, due to clogged oil guns, only four burners were capable of firing oil. Thus, as shown in Table 1, the tests were conducted while firing approximately a 36/64 mixture (by heat input) of oil and reabsorber gas. The oil composition changed very little, but the reabsorber gas composition varied slightly between the baseline and low-NO_x tests.

Table 1 also shows that, except for the percentage of excess air supplied, the heater was operated under very similar conditions during the two tests. Based on the O_2 concentration in the exhaust gas and the fuel composition, excess air was reduced from 22 percent in the baseline test to 17 percent in the low-NO_x test. The data indicated no significant change in heater operation as a result of the change to the low-NO_x configuration.

Emission Measurements and Results

The sampling and analysis procedures used in the tests conformed to a modified EPA Level 1 protocol for gas streams. Flue gas was measured at the stack, about 6 stack diameters downstream of the damper. These measurements included:

- Continuous monitoring for O_2, CO_2, CO, SO_2, and NO_x.
- SASS train sampling.
- Controlled condensation system (CCS) for SO_2 and SO_3.
- EPA Method 5 for particulates.
- Grab sample for onsite analysis of C_1-C_6 hydrocarbons by GC.
- Grab sample for N_2O analysis.
- Analyzing the filter catch, ashed XAD-2 resin, and the first impinger solution for 70 trace elements using SSMS and for Hg using AAS.
- Analyzing the second and third impinger solutions for Hg, As, and Sb using AAS.
- Extracting the XAD-2 sorbent resin with methylene chloride, concentrating the extract, then determining the organic content of the extract in two boiling point ranges: 100 to 300 °C by total chromatographable organics (TCO) analysis and >300°C by gravimetry (Grav).
- Further concentrating the extract and analyzing for the 58 semivolatile organic priority pollutants by GC/MS.
- IR analysis of the SASS filter, XAD-2 extract, and organic module condensate to identify organic functional groups.
- Direct insertion probe LRMS of the XAD-2 extract to identify compound categories present.
- Determining the alpha, beta, and gamma radiometric activity of the SASS filter.
- Level 1 Ames mutagenicity and CHO cytotoxicity bioassay tests of the XAD-2 sorbent extract.

Table 2 summarizes exhaust gas emissions measured in the test program. Emissions are presented in both nanograms per Joule heat input (ng/J) and micrograms per dry standard cubic meter of flue gas (μg/dscm). As a measure of the relative potential significance of the emissions for further analyses, the Threshold Limit Value (TLV) for each species is also noted in Table 2. Only species emitted at levels exceeding 10 percent of their TLVs are noted in the table.

Table 3 summarizes organic emission from the baseline and low-NO_x tests. In both tests, C_1 to C_6 hydrocarbons accounted for the largest fraction of organic emissions (95 percent for baseline and 82 percent for low-NO_x).

LRMS analyses of the XAD-2 extracts indicated that the organic emissions contained several compound categories, listed in Table 4 along with their estimated emission levels. In addition, 11 semivolatile organic priority pollutant compounds were identified by GC/MS analysis of the XAD-2 extracts. Table 5 lists the compounds and their concentrations measured during the two tests.

Radionuclide emissions were measured by determining the alpha, beta, and gamma radiometric activities of the flyash particulate samples. In both tests, the activities of the particulate samples were less than or equal to that of the blanks, indicating no significant radionuclide emissions.

Health effects bioassays were performed on the organic sorbent (XAD-2) module extracts from both tests. The bioassay tests performed were the Ames mutagenicity assay and the CHO cytotoxicity assay. The results of these tests, summarized in Table 6, suggest that the organic matter trapped by the XAD-2 sorbent is of moderate toxicity and moderate-to-high mutagenicity.

Conclusions

The use of staged air lances decreased NO_x emissions, with no significant adverse impacts. Particulate and organic emissions exhibited slight decreases, but trace element emissions exhibited an apparent increase which may be only

Table 1. Heater Operating Conditions

	Baseline	*Low NO_x*
Process rate, 1/s (bbl/day)	*21.5 (11,640)*	*21.5 (11,640)*
Reabsorber gas		
Flowrate, m^3/min (scfm)	*7.1 (251)*	*7.1 (251)*
Heat input, MW (million Btu/hr)	*8.35 (28.5)*	*8.13 (27.7)*
Fuel oil		
Flowrate, kg/min (lb/min)	*6.59 (14.5)*	*6.55 (14.4)*
Heat input, MW (million Btu/hr)	*4.77 (16.3)*	*4.75 (16.2)*
Temperatures, °C (°F)		
Crude in	*196 (384)*	*196 (384)*
Crude out (east)	*338 (641)*	*339 (642)*
Crude out (west)	*336 (637)*	*339 (642)*
Pressures, kPa (psig)		
Crude in (east)	*960 (140)*	*960 (140)*
Crude in (west)	*896 (130)*	*896 (130)*
Crude out	*227 (33)*	*234 (34)*
Burner - oil[a]	*324 (47)*	*324 (47)*
Burner - steam[a]	*537 (78)*	*537 (78)*
Burner - gas[b]	*30 (4.4)*	*30 (4.3)*
Gas pressure to heater	*234 (34)*	*241 (35)*
Excess air, percent[c]	*22*	*17*

[a]*Average of four burners using oil.*
[b]*Average of all six burners.*
[c]*Calculated from fuel analyses and flue gas O_2 measurements.*

Table 2. *Summary of Exhaust Gas Emissions*[a]

	Average Emission				Occupational Exposure Guideline (TLV)
	Baseline		Low NO_x		
	ng/J	μg/dscm	ng/J	μg/dscm	μg/m³
Criteria Pollutant and Other Vapor Species[a]					
SO_2	128	480,000	118	470,000	5,000
NO_x (as NO_2)	83	308,000	56	219,000	6,000
N_2O	27	100,000	15	59,000	--
SO_3	2.1	8,000	1.5	6,000	--
CO	1.19	4,400	0.99	4,000	55,000
Particulate	8.35	31,000	5.0	20,000	--
Gravimetric organic (Grav)	0.11	400	0.13	500	--
Total chromatographable organic (TCO)	0.11	400	0.022	90	--
Trace Elements					
Silver, Ag	9.8×10^{-7}	0.0036	0.0017	6.8	10
Potassium, K[b]	0.030	110	0.277	1,100	2,000
Sodium, Na[b]	>0.24	>910	>0.17	>690	2,000
Phosphorus, P	3.2×10^{-6}	0.012	0.0083	33	100
Nickel, Ni	>0.0081	>3.0	0.0073	29	100
Copper, Cu	0.0020	7.4	0.013	52	200
Iron, Fe	0.0076	28	0.048	190	1,000
Calcium, Ca[b]	$<1.0 \times 10^{-6}$	<0.004	0.096	380	2,000

[a]The O_2 and CO_2 concentrations were 4.0 and 12.1 percent, respectively for the baseline test and 3.3 and 11.7 percent for the low-NO_x test.
[b]True value is probably higher; at least one component of the SASS train showed a sample and blank concentration higher than the upper quantification limit.

Table 3. *Summary of Total Organic Emissions*

Organic Emissions	Baseline mg/dscm	Low NO_x mg/dscm
Volatile organic gases analyzed in the field by GC:		
C_1	0	0
C_2	3.6	2.8
C_3	4.8	0
C_4	6.4	0
C_5	1.5	0
C_6	0	0
Total C_1-C_6	16.3	2.8
Semivolatile organic material analyzed by TCO:		
XAD-2	0.36	0.06
Organic module condensate	<0.001	0.02
Total C_7-C_{16}	0.36	0.08
Nonvolatile organic material analyzed by Grav:		
Filter	<0.2	<0.3
XAD-2	0.4	0.3
Organic module condensate	<0.1	0.2
Total C_{16+}	0.4	0.5
Total organics	17.1	3.4

partially attributable to increases in the fuel trace element concentrations. Bioassay results of XAD-2 extracts indicated that the extracts were of moderate toxicity for both tests although the mutagenicity of the extracts increased from moderate (for the baseline test) to high (for the low-NO_x test).

Table 4. *Summary of LRMS Analyses*

Species Category	Intensity	Estimated Flue Gas Concentration mg/dscm
Baseline: TCO + Grav = 0.76 mg/dscm		
Ethers	100	0.22
Carboxylic acids	100	0.22
Heterocyclic sulfur compounds	100	0.22
Alkyl halides	10	0.02
Alcohols	10	0.02
Nitriles	10	0.02
Aromatic hydrocarbons	10	0.02
Heterocyclic nitrogen compounds	10	0.02
Total	350	0.76
Low NO_x: TCO + Grav = 0.35 mg/dscm		
Aliphatic hydrocarbons	100	0.16
Amines	100	0.16
Carboxylic acids	10	0.02
Aromatic hydrocarbons	10	0.02
Total	220	0.36

Table 5. *Results of GC/MS Analyses*

		Low NO_x µg/dscm		
Species	µg/dscm	Run 1	Run 2	Average
Phenol	1.0	0.20	0.55	0.4
Naphthalene	<0.04	0.40	0.78	0.6
1,3-dichlorobenzene	0.08	<0.04	<0.04	<0.04
1,4-dichlorobenzene	0.04	0.04	0.08	0.06
1,2-dichlorobenzene	0.1	<0.04	<0.04	<0.04
Nitrobenzene	0.2	0.04	0.08	0.06
2-nitrophenol	<0.2	0.43	0.39	0.41
Diphenylamine	0 1	0.08	0.08	0.08
1,2-diphenylhydrazine (as azobenzene)	1.4	<0.04	0.04	0.04
Phenanthrene	1.2	0.10	0.20	0.15
2,6-dinitrotoluene	<0.04	0.10	<0.04	0.07
Other polynuclears	<0.04	<0.04	<0.04	<0.04

Table 6. *Bioassay Results of XAD-2 Extracts*

	Bioassay	
Test	Ames[a]	CHO[b]
Baseline	M	M
Low NO_x	H	M

[a]M = Moderate mutagenicity, H = High mutagenicity.
[b]M = Moderate toxicity.

☆U. S. GOVERNMENT PRINTING OFFICE: 1984/759-102/10675

R. DeRosier is with Acurex Corporation, Mountain View, CA 94039.
***Robert E. Hall** is the EPA Project Officer (see below).*
The complete report consists of two volumes, entitled "Environmental Assessment of a Crude-Oil Heater Using Staged Air Lances for NO_x Control:"
"Volume I. Technical Results," (Order No. PB 84-223 031; Cost: $13.00)
"Volume II. Data Supplement," (Order No. PB 84-223 049; Cost: $22.00)
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The EPA Project Officer can be contacted at:
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