



Project Summary

Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner

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The report discusses emission results obtained from sampling the flue gas from an enhanced oil recovery steam generator equipped with a Mitsubishi Heavy Industries (MHI) PM low-NO_x crude oil burner. The test program performed included burner performance/emission mapping tests, comparative performance testing of an identical steamer equipped with a conventional burner, and comprehensive testing of the low-NO_x-burner-equipped steamer at a nominal low-NO_x setting. Emission measurements for the comprehensive tests 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 and specific quantitation of the semivolatile organic priority pollutant species and other major semivolatile organics; C₁ to C₆ hydrocarbon sampling; Method 5 particulate sampling; Method 8 sampling for SO₂ and SO₃ emissions; emitted particle size distribution measurements using Andersen impactors; and N₂O emission sampling.

Full load NO_x emissions of 110 ppm (corrected to 3 percent O₂) could be maintained from the low-NO_x burner at acceptable CO and smoke emissions. This compares to emissions of about 300 ppm (3 percent O₂) measured from the conventional burner equipped steamer, again at acceptable CO and smoke emissions.

Comprehensive tests were performed at a burner operating condition giving NO_x and CO emissions of 106 and 93 ppm, respectively, with flue gas O₂ of 3.0 per-

cent. Under these conditions, SO₂ and SO₃ emissions were 594 and 3.1 ppm, respectively. Particulate emissions were 39 mg/dscm with a mean particle diameter of 3 to 4 μm (two impactor runs). Total organic emissions were 11.1 mg/dscm and almost exclusively volatile (C₁ to C₆) organics.

Of the polynuclear aromatic hydrocarbons analyzed for, only naphthalene (1.4 μg/dscm), phenanthrene (0.3 μg/dscm), and pyrene (0.11 μg/dscm) were detected. Other semivolatile ketones and oxygenated aromatics were measured at levels ranging from 0.1 to 34 μg/dscm.

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

The petroleum reserves which can be recovered through primary production methods have been essentially exhausted in many of the older oil fields in the U.S. Remaining reserves in these regions are increasingly being produced through what have been termed enhanced oil recovery (EOR) methods. A popular EOR technique involves injecting steam into a field to lower the viscosity of the remaining crude so that it can be recovered. This steam for injection is raised by crude-oil-fired steam generators. Since the aggregate NO_x emissions from many steamers in a region can be significant, they have received

close regulatory attention in some regions, notably Kern County, California.

In an effort to reduce NO_x emissions from EOR steamers, burner manufacturers have experimented with low-NO_x burner designs. One such burner has been developed in Japan by MHI and is currently offered in the U.S. by CE-Natco, a steamer manufacturer.

A steamer equipped with an MHI low-NO_x burner was subjected to burner performance tests and comprehensive emission testing. In addition, another steamer equipped with a conventional burner was subjected to abbreviated emission testing for emission comparisons. Results of these tests are summarized in this report.

Summary and Conclusions

Source Description

Tests were performed on two CE-Natco model STOF steam generators rated at 15 MW (50 × 10⁶ Btu/hr) heat output. One unit was equipped with a conventional North American burner; the other had been retrofitted with an MHI PM low-NO_x burner.

The MHI PM burner, shown schematically in Figure 1, uses a split flame arrangement, whereby an inner air-deficient diffusion flame is separated from an outer air-rich premix flame by a blanket of recirculated flue gas. This arrangement produces NO_x levels significantly lower than those from conventional burners. A certain amount of staged overfire air (OFA), typically 10 percent, is injected about half-way down the length of the cylindrical furnace through three sets of three ports each, located at about the 4, 8, and 12 o'clock positions. This OFA ensures that sufficient excess air and mixing are achieved prior to the combustion gas's leaving the furnace.

Test Program

A limited set of flue gas emission tests were performed on the conventional-burner-equipped steamer. In these tests, flue gas emissions were measured at two steamer loads (full and 75 percent) while varying the overall excess air level. Next, the low-NO_x-burner-equipped steamer was subjected to relatively detailed burner performance testing. In these tests, flue gas emissions were measured while varying the burner operating parameter settings at full load. The burner parameters varied were the flue gas recirculation (FGR) rate; the relative distribution of combustion air to the premixed flame nozzles,

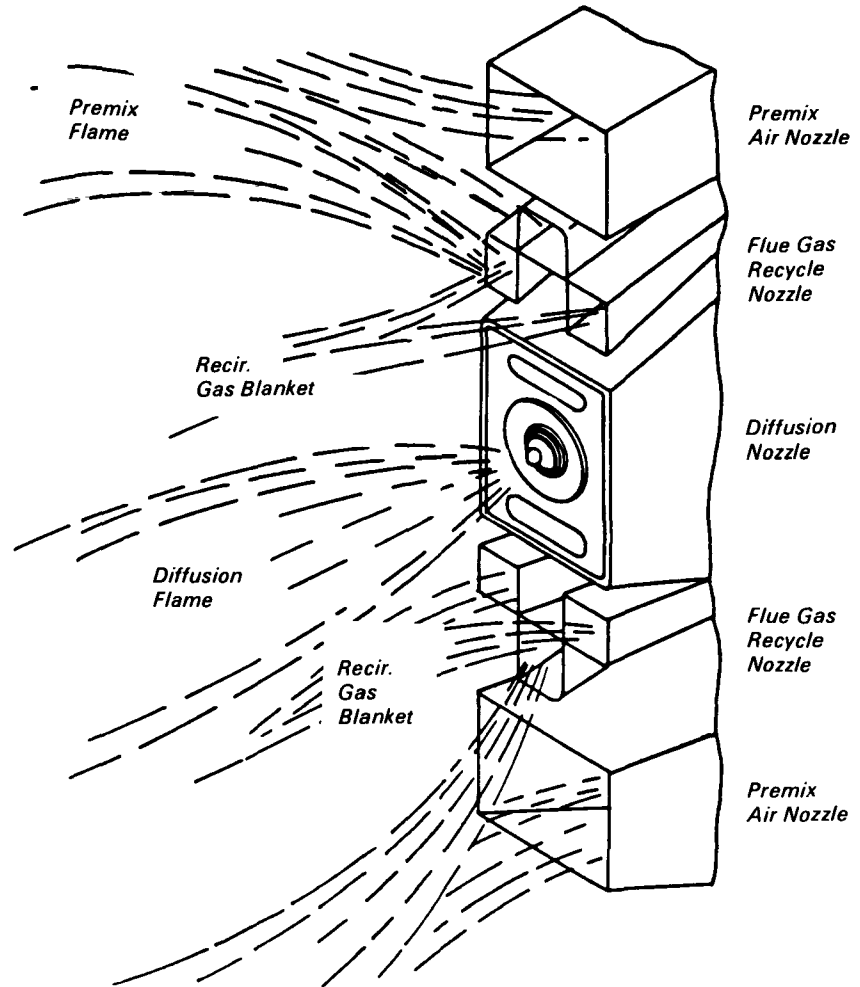


Figure 1. The MHI PM burner nozzle.

the diffusion flame nozzle, and the OFA ports; and the overall excess air level.

Finally, comprehensive emission testing was performed on the low-NO_x-burner-equipped steamer with the burner set at a nominal low-NO_x condition. The sampling and analysis procedures for these comprehensive tests conformed to a modified EPA Level 1 protocol. The measurements included:

- Continuous monitoring for NO_x, CO, CO₂, O₂, and total unburned hydrocarbon (TUHC)
- Source assessment sampling system (SASS) training sampling
- EPA Method 5 sampling for solid particulate
- EPA Method 8 sampling for sulfur oxides (SO₂ and SO₃)

- Particle size distribution measurements using Andersen impactors
- Grab sampling for onsite gas chromatographic analysis of volatile organics with boiling points in the C₁ to C₆ range
- Grab sampling for laboratory gas chromatographic analysis of N₂O

The analysis protocol for SASS train samples included:

- Analyzing methylene chloride extracts of particulate and XAD-2 resin for total organic content in two boiling point ranges: semivolatile organics with boiling points between 100 and 300 °C (nominally C₇ to C₁₆ organics) by total chromatographable organic (TCO) analysis, and non-volatile organics with boiling points

greater than 300 °C (nominally C₁₆₊ organics) by gravimetry

- Obtaining infrared (IR) spectra of the gravimetric residue of all extract samples
- Analyzing all extract samples for 58 semivolatile organic priority pollutants, including 16 polynuclear aromatic hydrocarbon (PAH) species by gas chromatography/mass spectrometry (GC/MS) according to EPA Method 625, with further identification and quantitation of major peaks in the GC chromatogram
- Analyzing selected extracts for general compound category composition by direct insertion probe low resolution mass spectrometry (LRMS)

Performance/Emission Tests Results

Results of the limited emission tests on the conventional-burner-equipped steamer are summarized in Figure 2 which shows stack NO_x emissions versus flue gas O₂ at the two steamer loads. The figure indicates a steady decrease in NO_x emissions as excess air is reduced until flue gas O₂ falls below about 3 percent. Below this O₂ level, the rate of NO_x emissions decrease increases. However, smoke emissions (Bacharach smoke number) also increased rapidly at flue gas O₂ below about 3.5 percent. For practical (acceptable CO and smoke emissions) operation, NO_x emissions of 300 ppm (corrected to 3 percent O₂) at flue gas O₂ of 3.7 percent were attainable at full load. At 75 percent load, NO_x emissions are reduced to about 250 ppm (3 percent O₂) at flue gas O₂ of 4.0 percent.

Results of the low-NO_x burner detailed performance evaluation tests are summarized in Table 1. Emission levels measured at the furnace outlet (by host site personnel) and at the stack downstream of the economizer section are shown. As noted, NO_x emissions from the unit varied from 95 to 180 ppm (corrected to 3 percent O₂) with changes in the parameters investigated. Certain conditions resulted in NO_x emissions at the stack below 100 ppm (3 percent O₂, dry) but these were, in general, accompanied by high CO emissions and high smoke spot. Conditions which resulted in NO_x of about 110 ppm with moderate CO and smoke might be considered as reflecting burner capabilities for realistic NO_x reductions.

Figures 2 and 3 illustrate the dependence of NO_x and CO at the stack on flue gas O₂. Both low-NO_x and conventional burner test data are shown. Figure 2 shows that the NO_x emissions from the low-NO_x burner were 45 to 65 percent lower than from the conventional burner at a given flue gas O₂. Figure 3 shows that CO emissions from the low-NO_x burner increased steeply at flue gas O₂ below 2.5 to 3.0 percent. This contrasts with conventional burner behavior where CO emissions were still low at flue gas O₂ down to 2.5 percent. These higher CO levels from the low-NO_x burner, which were accompanied by high smoke spots (see Table 1), are attributed to flame impingement which was observed at virtually all burner settings. Higher CO levels are attributed to increased flame impingement and excessively low diffusion zone stoichiometries during low O₂ and high OFA tests.

The effect of OFA flowrate on both CO and NO_x levels is illustrated in Figure 4. CO levels decrease sharply at OFA rates below 10 percent. At 3 percent OFA, CO levels are nearly those of the conventional burner (see Figure 3). NO_x emissions at minimum OFA, however, are not significantly higher than those at high OFA rates.

The effect of the flue gas recirculation (FGR) rate on NO_x and CO emissions is shown in Figure 5. FGR had a greater ef-

fect at higher O₂ and lower OFA levels (4.2 percent O₂ and 8 percent OFA) than it did at lower O₂ and higher OFA levels (2.6 percent O₂ and 19 percent OFA). That CO responded in an opposite manner can be explained in part by the greater mixing occurring at higher burner stoichiometries combined with lower FGR rates. This mixing tended to partly cancel the low-NO_x properties of the split frame. Conversely, that higher FGR rates combined with lower burner stoichiometry, while keeping the flames separate, caused greater impingement of the premix flame, which increased the CO levels.

Comprehensive Emission Test Results

Following these performance tests, operating conditions were selected for comprehensive emission testing using the SASS train and other aspects of the sampling protocol noted above. This test was conducted at 9.5 percent FGR, 10 percent OFA, about 54 percent premix air, and 36 percent diffusion air (test No. 21 in Table 1).

Table 2 summarizes the gaseous and particulate emission levels measured during these tests. Continuous monitor measurements at both the stack and the furnace outlet (provided by host site personnel) are shown. As indicated, stack NO_x and CO emissions averaged 106 ppm and 93 ppm, respectively, with smoke

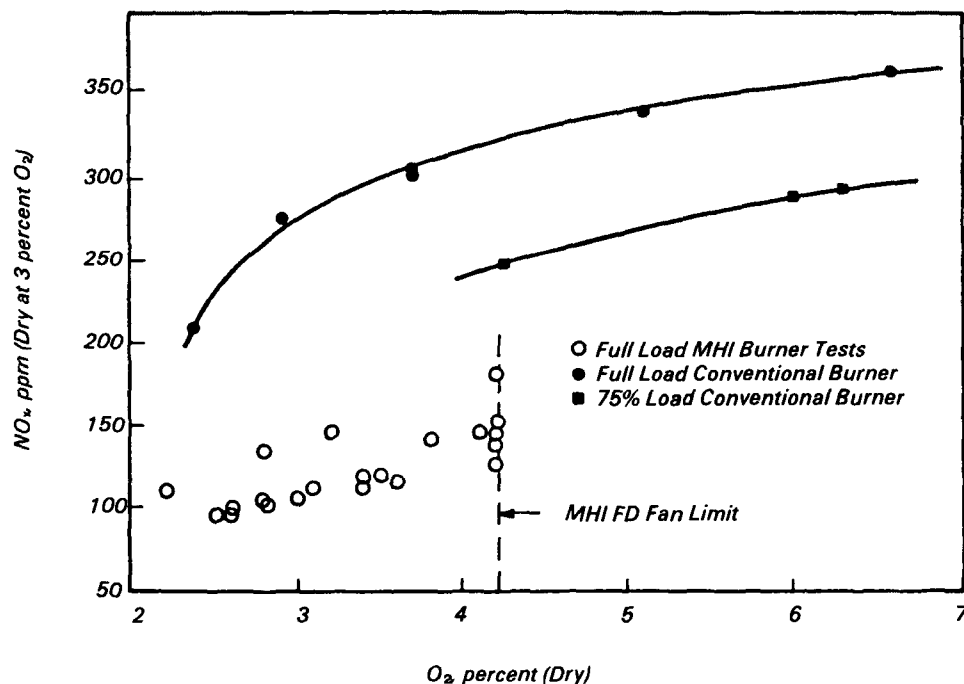


Figure 2. NO_x emissions versus flue gas O₂.

Table 1. MHI Burner Performance Test Results

Test No.	Air Distribution				Fuel Rate		Heat Input		Stack ^b					Furnace outlet ^c					
	FGR Rate (%)	OFA (%)	Premix ^a Flame Air (%)	Diffusion ^a Flame Air (%)	(l/s)	(BPD)	(MW)	(Million Btu/hr)	O ₂ (%)	CO ₂ (%)	CO (ppm) ^d	NO _x (ppm) ^d	TUHC (ppm) ^d	Smoke No.	O ₂ (%)	CO (ppm) ^d	CO ₂ (%)	NO _x (ppm) ^d	SO ₂ (ppm) ^d
1	8.9	19	48	33	0.383	208	16.1	55.0	3.5	13.4	99	119	3.2	>10	4.3	70	12.9	124	597
2	9.4	18	52	30	0.385	209	16.2	55.2	2.7	13.9	266	102	4.4	10	3.3	80	13.9	113	594
3	13.4	19	52	29	0.381	207	16.0	54.7	2.6	13.9	215	99	3.2	9.5	3.1	80	13.9	108	582
4	9.9	19	53	29	0.390	212	16.4	56.0	2.5	14.0	236	95	5.3	10	3.1	73	14.0	109	592
5	9.9	13	52	35	0.379	206	16.0	54.5	2.6	14.0	269	97	3.9	8	3.0	76	13.9	105	576
6	9.4	15	51	34	0.377	205	15.9	54.2	3.4	13.9	60	119	2.2	6	4.0	59	13.0	126	573
7	8.8	15	51	34	0.388	211	16.3	55.8	3.8	13.3	60	140	1.4	3.5	4.4	44	12.9	140	581
8	9.1	11	56	33	0.386	210	16.3	55.5	3.2	13.2	51	145	1.1	3.5	3.3	45	13.9	144	568
9	9.8	9	57	34	0.386	210	16.3	55.5	2.2	14.6	79	110	1.0	8	2.3	58	14.5	112	585
10	9.3	8	57	35	0.388	211	16.3	55.8	3.1	13.3	141	111	4.5	10	2.2	104	14.7	102	616
11	8.8	8	57	35	0.386	210	16.3	55.5	4.1	12.5	70	145	8.5	6	3.2	54	13.8	126	595
12	8.2	8	58	34	0.396	215	16.7	56.8	4.2	12.5	64	180	8.6	3.5	4.2	46	12.9	174	570
13	8.4	8	55	37	0.388	211	16.3	55.8	4.2	12.4	51	126	1.8	4	4.6	55	12.5	125	587
14	8.8	8	55	37	0.390	212	16.4	56.0	3.4	13.0	85	111	1.1	8	3.6	67	13.5	114	573
15	6.6	8	55	37	0.390	212	16.4	56.0	4.2	12.3	66	131	1.4	6	4.5	58	12.7	131	572
16	2.6	8	55	37	0.390	212	16.4	56.0	4.2	12.3	54	152	1.1	2.5	4.6	53	12.6	149	582
17	8.4	7	59	34	0.405	220	17.0	58.2	4.2	12.6	60	143	1.4	4	4.1	50	13.1	144	556
18	9.1	6	58	36	0.377	205	15.9	54.2	3.6	12.9	62	116	0.5	6	3.3	64	13.8	113	558
19	9.8	7	58	35	0.386	210	16.3	55.5	2.8	13.5	80	106	0	8	2.3	87	14.5	98	574
20	9.8	3	62	35	0.388	211	16.3	55.8	2.8	13.6	64	133	0	6	2.5	55	14.5	126	583
21 ^e	9.5	10	54	36	0.386	210	16.3	55.5	3.0	13.3	93	106	0	8	2.5	68	14.5	108	586

^a Premix and diffusion nozzle combustion air flows were not measured. Values shown here were estimated based on blower discharge pressure and static pressure readings in the windbox for diffusion and premix zones.

^b Emission measurements by Acurex.

^c Emission measurements by Getty Oil Company.

^d Dry at 3 percent O₂.

^e Using SASS train.

spot of 8 and flue gas O₂ of 3.0 percent. SO₂ and SO₃ emissions were 594 and 3.1 ppm, respectively, by Method 8; the SO₂ result agrees well with the furnace outlet continuous monitor. Method 5 particulate load was 39 mg/dscm. The Andersen particle-sizing measurements indicated that mean (50 percent cut point) particle size was between 3 and 4 μm (two runs).

Table 3 summarizes measured organic emissions from the low-NO_x burner-equipped steamer by organic boiling point range. The organic emissions are dominated by the volatile (C₁ to C₆) fraction, which is composed primarily of compounds in the C₃ and C₄ boiling range. No semivolatile organics were detected. However, nonvolatile organics (nominally C₁₆₊) were found in the particulate, though not in the sorbent module. This confirms the high smoke emissions for the tests and suggests that soot was forming.

Table 4 summarizes the PAH and other semivolatile organic priority pollutant species identified by GC/MS analysis. Also noted in the table are levels of other organic species identified and quantitated in the GC/MS sample analyses. Of the PAHs, only naphthalene, phenanthrene, and pyrene were found, and these only in

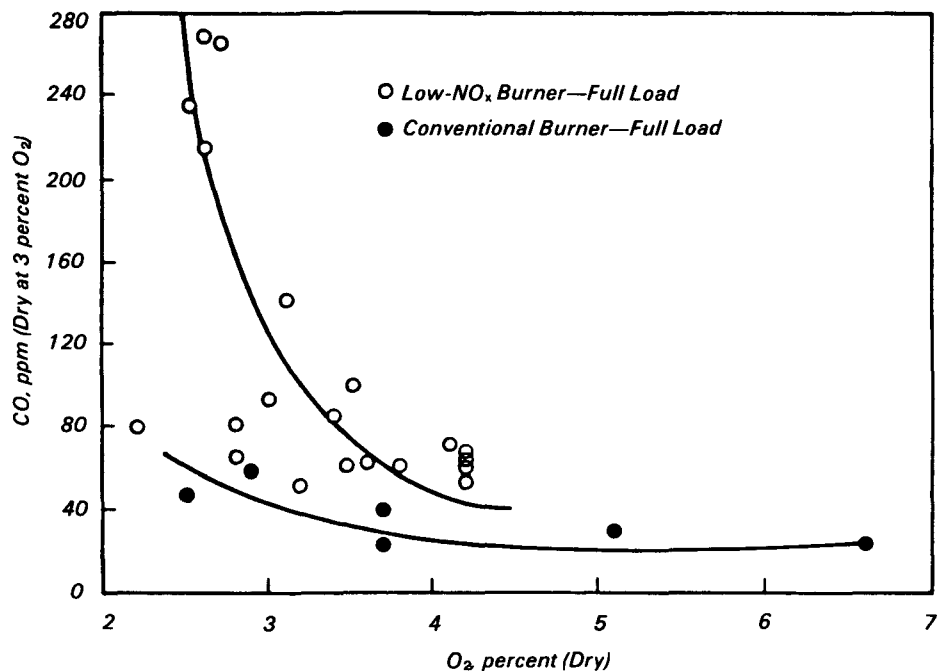


Figure 3. CO emissions versus flue gas O₂.

the particulate. The other species detected are generally oxygenated aromatics and fused-ring aromatics.

The flue gas N_2O levels measured in these tests, along with those measured in other tests performed in this EPA project, are summarized in Figure 6 which shows N_2O plotted versus corresponding NO_x emissions. It appears from Figure 6 that N_2O emissions are roughly proportional to a unit's NO_x emissions. A least squares fit of the data, which were taken from a range of combustion sources, suggests that N_2O emissions correspond to 22 percent of NO_x emissions, with a correlation coefficient (r^2) of 0.88. The curve in Figure 6 represents this fit.

Results of several quality assurance (QA) activities performed in these tests are discussed in Volume I of the project report. These results establish that the data quality was of an acceptable level in terms of the project's QA objectives.

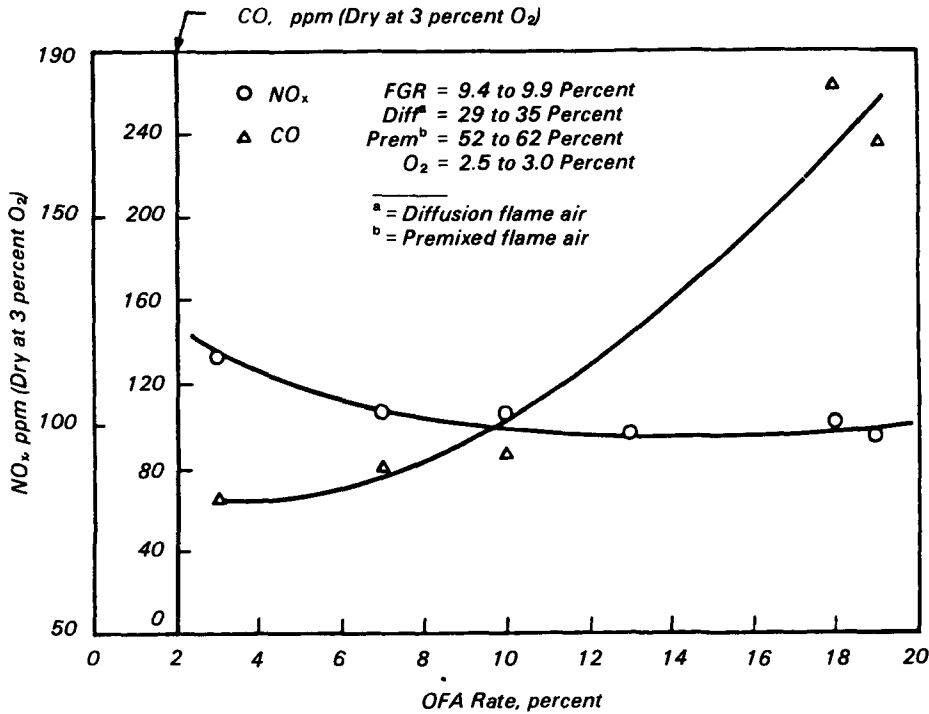


Figure 4. Effect of OFA rate on NO_x and CO emissions from the low- NO_x burner.

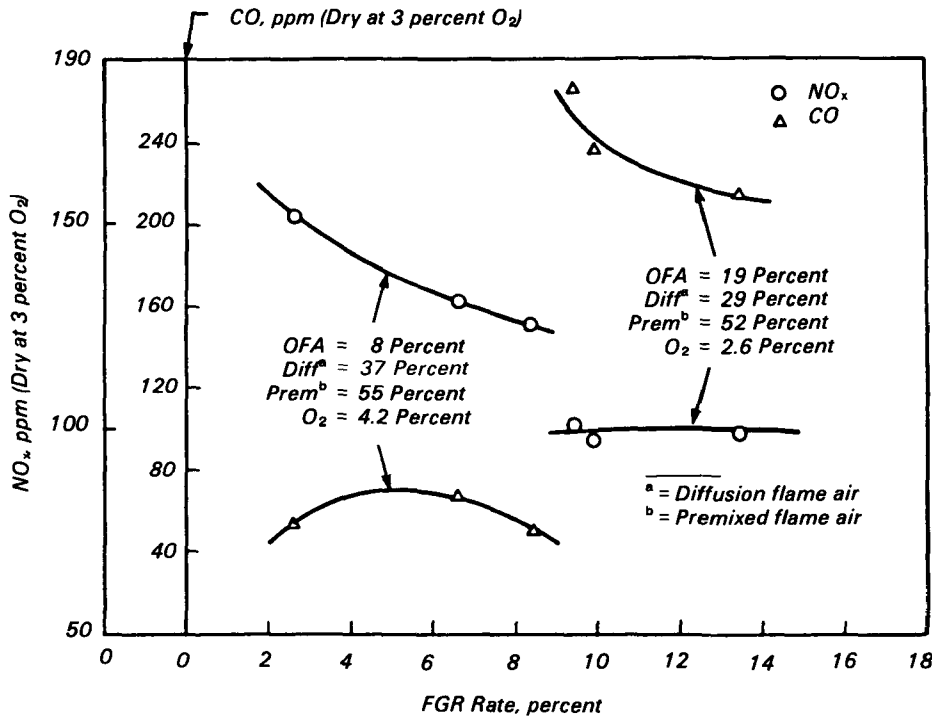


Figure 5. Effect of FGR rate on NO_x and CO emissions from the low- NO_x burner.

Table 2. Flue Gas Emissions

Pollutant	Stack ^a		Furnace outlet ^b			
	Range	Average	Range	Average		
<i>As measured:</i>						
O ₂ , percent dry	2.7 to 3.3	3.0	2.4 to 2.7	2.5		
CO ₂ , percent dry	13.1 to 13.5	13.3	14.4 to 14.5	14.4		
NO _x , ppm dry	108 to 115	106	110 to 112	111		
N ₂ O, ppm dry	12.9 to 20.5 ^c	17.0	— ^d	— ^d		
CO, ppm dry	45 to 135	93	68 to 75	71		
TUHC, ppm dry	<1	<1	— ^d	— ^d		
SO ₂ , ppm dry						
Continuous monitor	— ^d	— ^d	550 to 610	600		
Method 8	— ^e	594	— ^d	— ^d		
SO ₃ , ppm	— ^e	3.1	— ^d	— ^d		
Method 8						
Bacharach smoke number	8	8	— ^d	— ^d		
	ppm	ng/J ^f	lb/million Btu ^f	ppm	ng/J ^f	lb/million Btu ^f
Corrected to 3% O ₂						
NO _x (as NO ₂)	106	73.7	0.171	108	77.2	0.179
N ₂ O	17	11	0.026	— ^d	— ^d	— ^d
CO	93	39	0.091	69	29	0.069
TUHC (as CH ₄)	<1	<0.2	<0.001	— ^d	— ^d	— ^d
SO ₂						
Continuous monitor	— ^d	— ^d	— ^d	584	565	1.31
Method 8	594	574	1.34	— ^d	— ^d	— ^d
SO ₃ (as H ₂ SO ₄)						
Method 8	3.1	4.5	0.010	— ^d	— ^d	— ^d
Particulate	mg/dscm					
Method 5	39	14	0.033	— ^d	— ^d	— ^d
SASS	118	30	0.071	— ^d	— ^d	— ^d
Andersen	57 ^g	21 ^g	0.048 ^g	— ^d	— ^d	— ^d

^a Emission measurements by Acurex.

^b Emission measurements by Getty Oil Company.

^c Range over duplicate analysis of 6 separate gas samples.

^d Measurement not performed at this location.

^e Extractive sampling procedure, range not applicable.

^f Heat input basis.

^g Average of two trains run.

Table 3. Total Organic Emissions Summary

Organic Category	mg/dscm	ng/J
<i>Volatile organics analyzed in the field by gas chromatography</i>		
C ₁	0.2	0.07
C ₂	0	0
C ₃	8.4	3.0
C ₄	2.2	0.80
C ₅	0	0
C ₆	0	0
Total C ₁ -C ₆	10.8	3.9
<i>Semivolatile organics analyzed by TCO</i>		
Filter	—	—
XAD-2	<0.004	<0.001
Total C ₇ -C ₁₆	<0.004	<0.001
<i>Nonvolatile organics analyzed by gravimetry</i>		
Filter	0.3	0.11
XAD-2	<0.1	<0.04
Total C ₁₆₊	0.3	0.11
Total organics	11.1	4.0

Table 4. Compounds Detected in the CG/MS Analyses

Species	Filter (µg/g)	Particulate ^a (µg/dscm)	XAD-2 extract ^{a,b} (µg/dscm)	Total flue gas ^c (µg/dscm)
<i>Semivolatile organic priority pollutants</i>				
Naphthalene	1.6	0.19	1.2	1.4
Phenanthrene	2.6	0.30	<0.04	0.30
Phenol	1.9	0.22	<0.04	0.22
Pyrene	0.97	0.11	<0.04	0.11
<i>Other compounds identified</i>				
Benzofurandione	—	—	0.44	0.44
Benzoic acid	—	—	34	34
Benothiazole	28	3.3	—	3.3
Dichlorodibenzosulfone	—	—	0.52	0.52
Ethyl benzoate	—	—	0.40	0.40
Ethyl carbazole	110	13	—	13
Fluoren-9-one	180	20	—	20
Terphenyl	45	5.2	—	5.2

^a 28.0 dscm sampled, 3.11 g particulate on filter.

^b Average of duplicate injections.

^c Sum of average of duplicate XAD-2 result plus filter result.

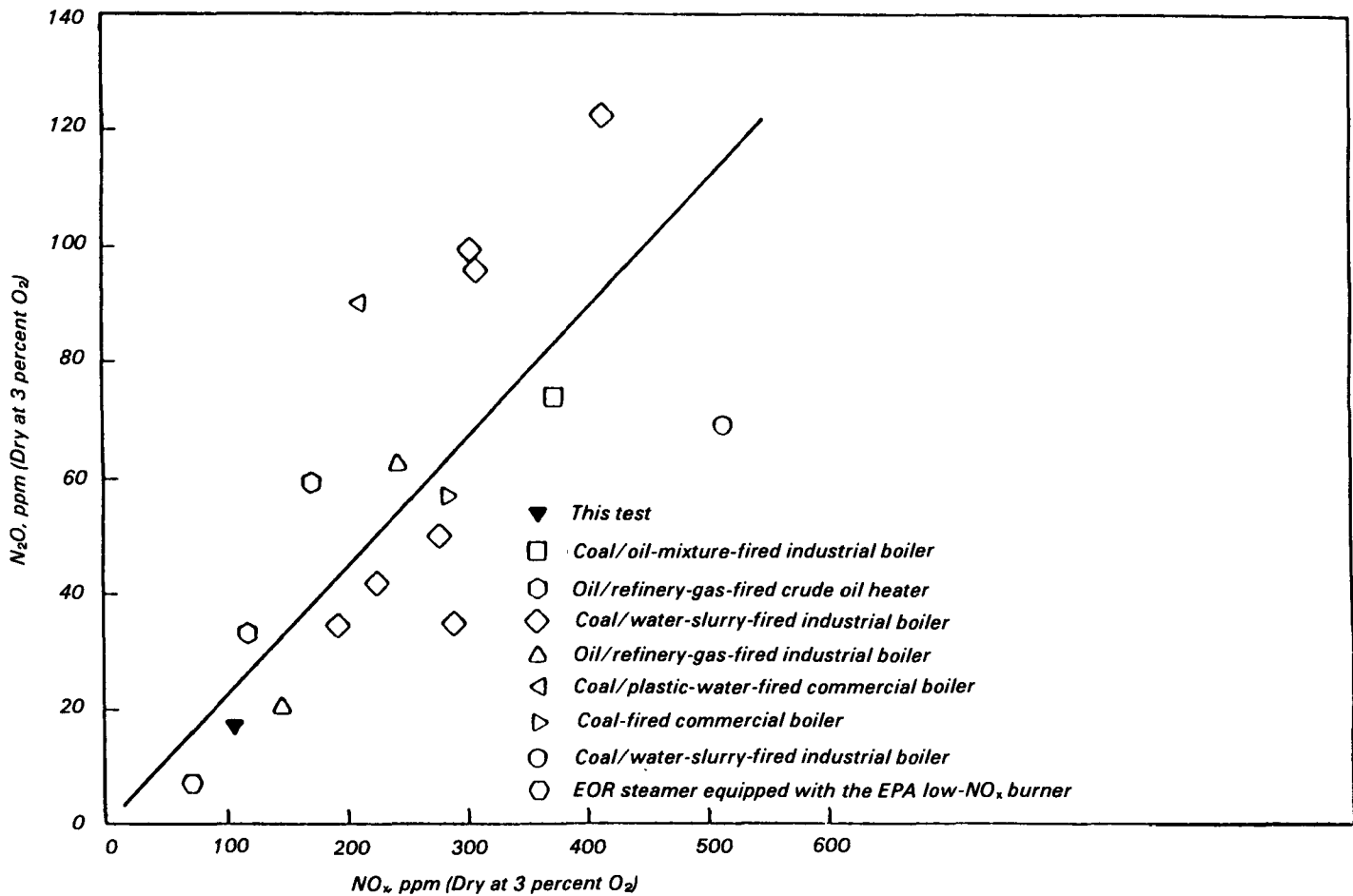


Figure 6. N₂O emissions from combustion sources as a function of NO_x emissions.

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The complete report consists of two volumes, entitled "Environmental Assessment of an Enhanced Oil Recovery Steam Generator Equipped with a Low-NO_x Burner:"

"Volume I. Technical Results," (Order No. PB 86-159 837/AS; Cost: \$11.95)

"Volume II. Data Supplement," (Order No. PB 86-183 290/AS; Cost: \$16.95)

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