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Pooled Source Emission Test Report: Gas-Fired IC Engines in Santa Barbara County

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Abstract

Fourteen natural gas-fired internal combustion (IC) engines were tested in Santa Barbara County, California in response to recent air toxics legislation. This testing was directed at engines in a variety of oilfield service applications, such as rod pump engines, compressor engines and water pump engines. The combustion exhaust was tested for formaldehyde, acetaldehyde, acrolein, benzene, toluene, xylenes, naphthalene, and polycyclic aromatic hydrocarbons. Additionally, the fuel was tested for aromatics to allow estimation of destruction efficiencies.

Two-stroke and four-stroke engines were tested. Four-stroke engines ranging in horsepower from 39 to 208 were utilized in pumping unit and constant load service. Emissions from the four-stroke engines were independent of size and service. Emissions from two-stroke engines were considerably higher than those from four-stroke engines.

Test results indicate that natural gas-fired IC engines do produce toxic substances in small amounts. Formaldehyde and benzene dominated the toxic emission profile. From the perspective of risk, other substances were insignificant.

Introduction

With the regulatory framework already in place for criteria pollutants such as NOx, SOx, and ROC, legislative focus is being directed toward toxic air emissions. Currently air toxics amendments to the Federal Clean Air Act are progressing through the House and the Senate. The oil industry can expect to be impacted by such legislation.

Various states have already developed air toxics regulations. California, New Jersey, and Illinois have implemented stringent air toxics regulations in recent years. From the standpoint of direct measurement requirements, the most rigorous is California's Air Toxics "Hot Spots" Information and Assessment Act, Assembly Bill (AB) 2588. AB 2588 is a right-to-know law that requires biennial test data on chemical releases into the air. The testing presented in this paper was performed in response to this law.

Though AB 2588 is a state law, much of the enforcement authority has been delegated to individual air districts. Air districts in California are either county-level or basin-wide entities that regulate a number of counties located in the same air basin. An example of a multi-county air district is the South Coast Air Quality Management District, with jurisdiction over the Los Angeles Air Basin.

The Santa Barbara County Air Pollution Control District (SBAPCD) has been among the most aggressive air districts in requiring direct measurement of suspected sources of air toxic emissions. The SBAPCD directed the oil and gas production industry operating in Santa Barbara County to quantify air toxics emissions from one of the principal combustion sources in oilfield use, natural gas-fired IC engines.

AB 2588 allows the use of "pooled" source testing data for substantially similar devices. The oil and gas production companies operating in Santa Barbara County opted to develop a pooled source testing program for gas-fired IC engines for two reasons:

- Minimize the cost of source testing to individual companies, and
- Improve data reliability by using a uniform testing approach with each engine type.

Scope of Test Program

Fourteen IC engines were tested for a limited number of volatile and semi-volatile organic compounds. Eight fuel gas samples were also tested for volatile organic compounds. Testing was directed toward two major compound types, aldehydes and aromatics. The aldehydes consisted of formaldehyde, acetaldehyde, and acrolein (see Figure 1). Aromatic compounds consisted of benzene, toluene, xylene, and polycyclic aromatic hydrocarbons (PAH). PAH are compounds composed of multiple benzene rings, and a total of 16 PAH compounds were tested (see Figure 2). Two major gas-fired IC engine types were tested: four-stroke and two-stroke engines.

The test program had four objectives:

1) Define distinct categories of gas-fired IC engines in oilfield service.

2) Quantify selected air toxics using approved California Air Resources Board (CARB) test methodologies.

3) Develop air toxic emission factors for each gas-fired IC engine category.

4) Evaluate the viability of naphthalene analysis from bag samples.

Engine Categories

The following engine characteristics were evaluated prior to separating engines into distinct categories:

- o Engine type: Four-stroke (rich burn) or two-stroke (lean burn)
- o Fuel: Field gas or pipeline gas
- o Application: Variable or constant load
- o Size: Greater or less than 100 hp
- o Control Equipment: None or pre-stratified charge

Eight distinct engine categories were identified in the aggregate engine population of participating companies. These engine categories are listed in Table 1.

Fuel Variability

Two general types of fuel were identified in the test program, "field" gas and "pipeline" gas. Field gas is naturally occurring gas that is separated from the crude oil production stream at the well and is used in onsite combustion processes with no further processing. The primary difference between field gas and pipeline gas is the CO_2 concentration, and to a lesser extent, the H_2S concentration. Field gas also generally has a greater concentration of higher molecular weight hydrocarbon gases than pipeline gas. CO_2 and H_2S concentration limits imposed on pipeline gas restrict the use of field gas to onsite combustion processes unless further gas processing is available, or unless field gas meets pipeline gas requirements without processing.

Combustion Process Variability

All compounds included in the test program are volatile or semi-volatile organic compounds. The formation and destruction mechanisms of these compounds in an IC engine environment are complex. These compounds can be present in the fuel gas delivered to the engine, and can also be formed as "products of incomplete combustion" (PICs) during fuel-rich combustion or as a result of poor fuel/air mixing in the intake manifold. The engine can potentially serve as an incinerator of fuel-bound organics while simultaneously generating these compounds as PICs.

TABLE 1

Engine Categories

Category Number	Engine Type	Fuel Gas Type	HP	Load
1	Rich burn	Pipeline	<100	Cyclic
2	Rich burn	Pipeline	>100	Cyclic
3	Rich burn	Pipeline	<100	Constant
4	Rich burn	Pipeline	>100	Constant
5	Rich burn	Field	<100	Cyclic
6	Rich burn	Field	>100	Cyclic
7	Rich burn	Field	<100	Constant
8	Lean burn	Field	>100	Constant

Test Methods

Approved CARB test methodologies were used to measure aldehydes, BTX and PAHs. Sampling was performed between April 10 and April 26, 1990. The whole air samples collected for BTX analyses were also used as a sample source for naphthalene. It was anticipated that naphthalene would be the predominant PAH compound present, as it is the most volatile compound in the PAH family. Whole air samples were analyzed for naphthalene to investigate the validity of this low-cost technique as an alternative to isokinetic PAH sampling. Simultaneous whole-air and isokinetic samples were taken at two test sites to allow for comparison of naphthalene results.

Aldehydes

CARB Method 430 was used to quantify formaldehyde, acetaldehyde, and acrolein. Triplicate samples were collected from the exhaust of each engine during consecutive 30-minute runs. A schematic of the aldehyde sampling train is shown in Figure 3. Aldehyde analyses were performed using high performance liquid chromatography (HPLC). All 14 engines were tested for formaldehyde, while 7 were also tested for acetaldehyde and acrolein.

Method 430 employs a series of two midget impingers filled with 2,4-dinitrophenylhydrazene (DNPH) through which exhaust gas is passed. Aldehydes react rapidly with DNPH in acidic solution to form hydrazones. This type of capture is preferred, as aldehydes readily decompose in whole air samples.

After organic solvent extraction, the aldehyde-DNPH derivative (hydrazone) is determined using reverse phase HPLC with ultraviolet (UV) absorption detection operated at a wavelength of 360 nanometers. Aldehydes in the sample are identified and quantified by comparison of retention time and area counts, respectively, with those of standard solutions. Table 2 lists the results from each test run.

Benzene, Toluene and Xylenes

Benzene, toluene, and xylene (BTX) were analyzed using CARB Method 410A. Duplicate samples were collected from each engine. Samples were collected in 12-liter Tedlar bags filled during consecutive 30-minute sampling periods. A schematic of the BTX sampling train is shown in Figure 4. Analyses by gas chromatography/photoionization detector (GC/PID) were performed within 72 hours of sampling. Table 3 lists average inlet and outlet benzene concentrations.

PAH

CARB Method 429 was used to quantify PAH emissions. Triplicate samples were collected during consecutive 2-hour sampling periods. Method 429 uses an isokinetic sampling train designed for the collection of semi-volatile organic compounds. A schematic of the PAH sampling train is shown in Figure 5. Particulate phase PAHs are collected in the front half of the sampling train, while gas phase PAHs are collected in a XAD resin cartridge and back half impingers. PAH samples were extracted in the laboratory and measured using low resolution mass spectroscopy (LRMS).

To perform isokinetic testing, a relatively constant velocity profile is necessary in the exhaust stack. This requirement limited the choice of Method 429 test sites to constant load engines. One 4-stroke and one 2-stroke engine were tested using Method 429. PAH emission factors developed from these two tests were then applied to the entire engine population, including both constant and variable load engines, as generic PAH emission factors. Table 4 lists the results of PAH testing performed on these two engines.

Naphthalene in Whole Air

Naphthalene analysis was performed using an HP 5890 gas chromatograph with an HP 5970 mass selective detector (GC/MS). Exhaust gas samples were cryogenically preconcentrated to allow for detection limits as low as 50 ppbv. Higher detection limits were recorded for fuel samples due to the concentrated hydrocarbon matrix characteristic of this sample type. Samples were obtained from the same Tedlar bags used for BTX analysis. Standards were prepared for exhaust gas samples over the range of 50 ppbv to 1 ppmv by injection of the appropriate amount of standard (0.05 molar solution of naphthalene in benzene) into 6-liter passivated summa canisters.

Test Results

Twelve 4-stroke and two 2-stroke engines were included in this test program. There was no apparent correlation of emissions to engine service or horsepower. Emissions correlated to engine type and BTX emissions correlated to fuel BTX content. There was no apparent correlation between BTX emissions and excess oxygen within the range of oxygen concentrations from 2.4 percent to 7.1 percent. However, the data indicate that BTX emissions substantially increased as the exhaust gas oxygen concentration approached zero. There was no apparent correlation between the use of pre-stratified charge for NO_x control and BTX emissions. The results for specific compound groups are discussed below.

Aldehydes

Aldehyde emissions did not correlate to fuel aldehyde content or exhaust gas oxygen concentration over the range investigated. The results are as follows:

	4-Stroke	2-Stroke
Formaldehyde:	25.7 lb/MMcf	52.6 lb/MMcf
Acetaldehyde:	3.9 lb/MMcf	6.2 lb/MMcf
Acrolein:	1.5 lb/MMcf	1.9 lb/MMcf

Two of the 36 four-stroke engine test runs were omitted as they were in excess of five standard deviations from the sample average.

Aromatic Compounds

Emissions from 12 four-stroke engines were measured in this test program. The test results for two of these engines are discussed separately below as they were operated near stoichiometric combustion conditions during testing. Results indicate that for engines with benzene fuel concentrations less than 1 lb/MMcf, there is no relation between BTX in the fuel and stack emission rates.

Benzene was the dominant aromatic compound present, representing 63 percent by weight with toluene, xylene, and naphthalene contributing 22 percent, 9 percent, and 6 percent, respectively. The data indicate that BTX emissions are present at the following minimum concentrations regardless of fuel BTX content:

Benzene	1.18 lb/MMcf
Total BTX	1.56 lb/MMcf

However, as the BTX fuel concentration increases, BTX emissions increase. This relation is depicted in Figures 6 and 7. It should be noted that the developed correlations are based on samples taken from two engines having an aromatic fuel content of 143 lbs/MMcf. With a BTX emission rate of 3.68 lb/MMcf, these tests indicate the BTX in the fuel is consumed by the combustion process with an efficiency of 97 percent. The benzene data yield a similar relation, with a benzene emission rate of 2.31 lb/MMcf and a fuel-benzene content of 60 lb/MMcf. Further testing is necessary to establish destruction efficiencies for intermediate BTX fuel concentrations.

For one engine operated at an excess oxygen concentration near zero, the data show extremely high BTX emissions. Substantially more data is needed to develop a "near stoichiometric" BTX

emission profile. The other engine operated at near stoichiometric conditions was firing propane, and therefore test results have not been compared to the results from natural gas-fired engines.

Aromatic compound emission rates decreased with increasing molecular complexity. While GC/MS analysis indicated the presence of naphthalene in some samples, it was not quantifiable to the detection limit of 50 ppb. However, the PAH test results did quantify naphthalene at 29 ppb for the one rich-burn engine tested. The naphthalene emission rate for this engine was 0.12 lb/MMcf. The most prevalent PAH following naphthalene was acenaphthylene, measured at 1.5 ppb. The emission rate of all "non-naphthalene" PAH is approximately 0.01 lb/MMcf.

The two 2-stroke engines were operating at about 14 percent excess oxygen during testing, and their average BTX emission rate was 13.3 lb/MMcf. This emission rate is approximately 6 times greater than the average for the four-stroke engines operating between 2.4 and 7.1 percent excess oxygen. The average BTX emission rate from the two-stroke engines was approximately one-half that of the "near stoichiometric" four-stroke engines.

Conclusions

A. Four-stroke engines: excess O_2 between 2.4 and 7.1 percent Assume 1000 Btu/scf of fuel

1. Emissions of formaldehyde and benzene averaged 25.7 and 1.45 lb/MMcf, respectively.

2. For fuels with BTX concentrations greater than 10 lb/MMcf, a BTX destruction efficiency range of 84 to 97 percent may be expected.

3. For fuels with BTX concentrations ranging from 0.4 to 1.5 lb/MMcf, emissions of BTX averaged 1.8 lb/MMcf. There is no apparent correlation between BTX emission rates and BTX fuel concentration when BTX fuel concentration is less than 1.5 lb/MMcf. The data indicate that the baseline BTX emission rate ranges from 1.3 lb/MMcf to 2.1 lb/MMcf for engines operated with sufficient excess oxygen to achieve relatively complete combustion.

BTX → & Benzene

B. Four-stroke engines: "near stoichiometric"

1.8 + 26.5

1. BTX emission rate averaged 26.5 lb/MMcf.

C. Two-stroke engines

1. BTX emission rate averaged 13.3 lb/MMcf.

D. All engine categories

1. PAH emission rates are negligible for PAH molecules larger than naphthalene.

2. Whole air sampling for naphthalene was found to be a viable technique to indicate that naphthalene was not emitted in significant quantities from the standpoint of AB 2588 reporting requirements, though a lower detection limit is necessary for accurate quantification using this technique.

Table 3

Benzene and BTX Emissions[1]

4-Stroke Engines	Service	BENZENE Out lb/MMcf	BENZENE In lb/MMcf	TOTAL BTX Out lb/MMcf	TOTAL BTX In lb/MMcf	% Oxygen
77 hp MM 336	Pumping Unit	1.13	0.72	1.67	1.51	6.00
77 hp MM 335	Pumping Unit	0.83	0.72	1.32	1.51	7.00
208 hp Wauk 1197	Pumping Unit	1.45	0.72	1.81	1.51	6.00
208 hp Wauk 1197	Pumping Unit	1.38	0.72	2.11	1.51	2.70
74 hp Wauk 145 w PSC	Inj. Pump	1.38	0.25	2.03	0.36	7.10
74 hp Wauk 145 w PSC	Inj. Pump	1.18	0.25	1.56	0.36	2.40
208 hp Wauk 1197	Inj. Pump	1.30	0.72	1.88	1.51	4.60
60 hp MM 605	Pumping Unit	2.38	59.68	3.83	143.15	4.50
60 hp MM 605	Pumping Unit	2.31	59.68	3.68	143.15	3.30
159 hp Wauk 1197	Pumping Unit	1.12	7.00	2.09	10.32	4.60
Near Stoichiometric Air/Fuel		Ag. 1.446.				
54 hp MM 425	Compressor	13.00	18.11	17.82	73.90	0.30
39 hp Wauk 195[2]	Water Pump	26.85	0.05	35.15	0.08	0.00
2-Stroke Engines		Ag 19.975				
150 hp Clark MA4	Compressor	13.83	53.51	20.48	68.21	14.20
660 hp Cooper Bessemer	Compressor	4.01	26.75	6.18	60.62	14.00

[1] Values presented are average of two runs per engine. Ag. - 8.92

[2] Propane-fired engine .00892 lb/MMBtu

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