

The Impact of Add-on Catalytic Devices on Pollutant Emissions from Unvented Kerosene Heaters

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The sales and use of portable unvented kerosene heaters have increased dramatically over the past decade. Many studies have documented pollutant emission rates from kerosene heaters.¹⁻⁷ Carbon monoxide (CO), carbon dioxide (CO₂), nitric oxide (NO), nitrogen dioxide (NO₂), formaldehyde (HCHO), suspended particles, and semivolatile and nonvolatile organic compounds, including some nitrated and non-nitrated polycyclic aromatic hydrocarbons (PAH), can be emitted by kerosene heaters.

Recently, several add-on catalytic devices designed to reduce some pollutant emissions have become commercially available. The tests described here were designed to measure the impact of these devices on pollutant emissions from unvented kerosene heaters. Emissions of CO, NO, NO₂, HCHO, and total suspended particles (TSP) were investigated in this study. In addition, analyses of particulate sulfur and chromium were conducted for some tests.

Experimental Methods

Heaters

Two unvented kerosene space heaters, one radiant and one convective, were used for this study. Each heater was operated in a low-flame and a high-flame mode. The fuel consumption rates for the radiant heater averaged 5600 kJ/h for the low setting and 6800 kJ/h for the high setting. For the convective heater, the fuel consumption rates averaged 11,400 kJ/h for the low setting and 14,900 kJ/h for the high setting. The heaters were fueled with low-sulfur kerosene containing less than 0.04 percent sulfur and rates 1-K.⁸

Catalytic Devices

Three catalytic devices, designated throughout the report as CAT1, CAT2, and CAT3, were used for the study. Table I describes each device. The manufacturer's instructions were followed when installing the catalysts. Hanging wires were used to position the device slightly above the flame of the kerosene heaters.

Test Protocol

Each heater in each burn mode (low and high) was tested without a catalytic device and then tested with each catalytic device in place at high and low burn rates. Each test was repeated to give a total of 32 tests conducted in a random sequence.

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A heater or heater/catalyst combination was placed on a rolling platform in a 27-m³ environmental chamber.⁹ The air exchange rate in the chamber was measured for all tests and ranged from 0.6 to 0.7 h⁻¹. The heater was operated inside the chamber until 5500 kJ (130 g or 0.16 L) of fuel was consumed to obtain an initial emission rate. Then the heater was rolled out of the chamber while still burning. After 1.5 hours, the heater was rolled back into the chamber, and a second 5500 kJ of fuel was consumed to obtain a steady-state emission rate. A more-detailed description of the test protocol is given elsewhere.^{9,10}

Air-Pollution Instrumentation

Most air-pollution monitoring instruments were contained in the Lawrence Berkeley Laboratory's Mobile Atmospheric Research Laboratory (MARL). The MARL is capable of remotely sampling CO, CO₂, NO, NO₂, and O₂ using state-of-the-art real-time pollutant analyzers. Details on the MARL instrumentation, sampling system, and calibration system are given elsewhere.¹¹

In addition to the instrumentation in the MARL, samplers for HCHO and TSP were located just outside the chamber. HCHO was collected in refrigerated bubblers and analyzed using the modified pararosaniline method.¹² TSP were collected inside and outside the chamber on two different filter media. Fluoropore filters (polytetrafluoroethylene bonded to high-density polyethylene) with a nominal pore size of 1.0 μm were used for gravimetric analyses. Millipore-type RA filters (mixture of cellulose acetate and cellulose nitrate) with a nominal pore size of 1.2 μm were used for chromium and sulfur analyses. Particulate chromium and sulfur concentrations were measured using x-ray fluorescence.¹³

Although TSP samples were collected, particle emissions from radiant kerosene heaters are in the respirable range (<2.5 μm) with a mass-median diameter of 0.09 μm (σ_g = 1.9).⁴ A similar result is expected for particles emitted from convective heaters. For calculation of emission rates, average indoor TSP and chromium particle concentrations were converted to pseudo real-time data by using the real-time submicrometer (<0.6 μm) particle data collected by an electrical aerosol size analyzer.¹⁴

Results and Discussion

Table II summarizes the pollutant emission-rate results without a catalyst (baseline condition) and with CAT1, CAT2, and CAT3 for CO, NO, NO₂, N (of NO_x), TSP, and HCHO. (For this analysis, NO_x is the sum of NO and NO₂).

Table I. Descriptions of add-on catalytic devices.

Device code name	Device description	Catalyst material description
CAT1	Element is a wire mesh (2 ply) over a 15-cm-diameter circular wire frame. Outer lip is 0.5 cm thick.	Platinum-coated wire mesh
CAT2	Element is a 13.5-cm-diameter disk ribbed with 1.0-cm-deep pleats. Metal holder is a conic section 18 cm in diameter on the bottom, 16 cm in diameter on the top, and 5.2 cm thick.	Platinum-coated pleated cloth
CAT3	Regular-size element (used for the radiant heater) is a disk 10 cm in diameter on the bottom, 12.0 cm in diameter on the top, and 2.8 cm thick. Large-size element (used for the convective heater) is a disk 11.8 cm in diameter and 1.3 cm thick. The metal holder is a conic section 19 cm in diameter on the bottom, 15 cm in diameter on the top, and 4.5 cm thick.	Honeycombed, porous, coated ceramic

Eight emission-rate measurements were made for each heater/catalyst combination tested. The eight measurements consisted of two initial and two steady-state tests at the low fuel consumption rate and two initial and two steady-state tests at the high fuel consumption rate. These emission-rate measurements were combined, and the geometric means and geometric standard deviations (GSDs) are presented (see Table II). A statistical analysis (*t*-test) of the effect of the catalysts on the heater emissions was conducted in log space on the grouped data. The cases in which the difference between average pollutant emission rates with and without a catalyst were statistically significant (at the 95 percent confidence level) are noted in Table II.

It is important to note that between-test variations and the time-dependent (initial compared with steady-state) variations of the pollutants emission rates were large in many cases.¹⁵ This effect results in several relatively large GSDs appearing in Table II. Consequently, firm conclusions

regarding the effect of the catalysts on the emissions rates of all pollutants under all conditions were precluded. However, several interesting trends are apparent.

All of the catalysts reduced CO emissions when inserted into the radiant heater; however, only CAT1 and CAT2 have a statistically significant effect on CO emissions from the radiant heater, reducing them by a factor of approximately two. None of the catalysts can be deemed effective in reducing CO emissions from the convective heater.

All catalysts in every heater/burn-rate configuration increased the NO emission rates, with the increases being statistically significant for the tests using the radiant heater. However, NO is not considered a pollutant with major health consequences.

The emission rates of NO₂, a pollutant with more-serious health consequences than NO, were reduced (statistically significant) by all three catalysts when they were used on the radiant heater. As with CO, CAT1 and CAT2 were more effective in reducing NO₂ emissions from the radiant heater than was CAT3. CAT1 and CAT2 increased NO₂ emissions from the convective heater; however, this increase was not statistically significant.

The effectiveness of the catalysts on the N (of NO_x) emission rates was negligible for radiant heater tests. In the convective heater tests, all three catalysts caused an increase in the N (of NO_x) emission rates, with the increase for CAT2 being statistically significant.

TSP emission rates were the most variable of all pollutant emission rates with GSDs ranging from 3.2 to 8.4. CAT2 and CAT3, and to a much lesser extent CAT1, have the potential for greatly increasing the TSP emission rate from the radiant heater. This must be considered a major drawback to using CAT2 and CAT3 for radiant heaters since the particles have the potential for containing harmful organic compounds.⁶ An increase in TSP emissions may also imply an increase in semivolatile organic-compound emissions; however, these compounds were not measured in this study.

A very small, statistically insignificant, reduction in HCHO emissions from the radiant heater was observed for all three catalysts. The use of the catalysts on the convective heater had almost no effect on HCHO emissions.

In addition to the pollutants described in Table II, particulate sulfur emissions were measured for most tests. At least one measurement was made for each heater/catalyst combination. Particulate sulfur levels inside the chamber were not elevated above background (outside) levels in any test (particulate sulfur emission rates were less than 0.2 μg/kJ for all tests). For comparison, sulfur dioxide emission rates from kerosene heaters that use 1-K fuel have been observed to range from 4 to 15 μg/kJ.^{1,5}

Table II. Emission rate test results^a from add-on catalytic devices for unvented kerosene heaters.

Catalytic device	CO (μg/kJ)	NO (μg/kJ)	NO ₂ (μg/kJ)	N (of NO _x) (μg/kJ)	TSP (μg/kJ)	HCHO (μg/kJ)
Radiant kerosene heater:						
Baseline	193 (1.38)	0.10 (1.7)	5.4 (1.14)	1.6 (1.15)	0.20 (3.20)	1.06 (1.45)
CAT1	76 (1.62) ^b	1.08 (1.5) ^b	2.8 (1.19) ^b	1.4 (1.19)	0.18 (8.40)	0.71 (2.20)
CAT2	74 (1.64) ^b	1.67 (1.4) ^b	2.4 (1.22) ^b	1.5 (1.20)	0.34 (6.27)	0.86 (1.66)
CAT3	144 (1.46)	0.50 (2.3) ^b	4.1 (1.13) ^b	1.5 (1.18)	0.53 (6.83)	0.96 (1.43)
Convective kerosene heater:						
Baseline	21 (2.37)	4.96 (1.5)	5.3 (1.84)	4.2 (1.32)	0.70 (7.61)	0.18 (1.92)
CAT1	17 (2.28)	6.55 (1.7)	7.0 (1.22)	5.4 (1.25) ^b	0.43 (6.41)	0.16 (1.92)
CAT2	18 (2.11)	6.82 (1.6)	6.1 (1.29)	5.3 (1.28)	0.54 (7.87)	0.19 (1.60)
CAT3	19 (2.01)	7.34 (1.6)	5.2 (1.30)	5.3 (1.24)	1.96 (6.85)	0.20 (1.98)

^a Results presented are the geometric mean and geometric standard deviation (in parentheses) from 8 emission-rate measurements (i.e., two repeats of a high-burner-setting test and a low-burner-setting test, with an initial and a steady-state emission rate measured in each test).

^b Significantly different from the baseline emission rate at the 95 percent confidence level.

Particulate chromium concentrations were elevated for all tests. This is in accordance with a previous study which found that trace amounts of particulate chromium were emitted from the burner assembly of a radiant kerosene heater.⁴ There was considerable variation in the chromium emission rate between repeat tests. This variation precluded any conclusions regarding the effect of using a catalyst on particulate chromium emission rates. The chromium emission rates across test types approximated a lognormal distribution with a geometric mean of 0.011 $\mu\text{g}/\text{kJ}$ and a large GSD of 5.0.

Conclusions

Add-on catalytic devices were moderately effective in reducing CO and NO₂ emissions from a radiant heater. Two of the three catalysts reduced these emissions by roughly 50 percent (statistically significant), whereas the third reduced them by roughly 25 percent (statistically insignificant). However, the TSP emissions increased, in general, with the use of these catalysts.

For convective heaters, the add-on catalysts moderately reduced CO emissions for most test types, but these reductions were statistically insignificant. However, two of the three catalysts increased NO₂ emissions, and the third catalyst increased TSP emissions. Average HCHO emissions were slightly reduced by the catalysts when the radiant heater was operated, but these reductions were not statistically significant.

Overall, the add-on catalysts tested in this study did not consistently lower the emission rates of the important pollutants measured; therefore, the authors cannot recommend use of these catalysts as an effective method for reducing pollutant emissions from unvented kerosene space heaters.

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