Title

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THE IMPACT OF ADD-ON CATALYTIC DEVICES ON POLLUTANT EMISSIONS FROM UNVENTED KEROSENE HEATERS

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Abstract

The impact of add-on catalytic devices on pollutant emissions from kerosene heaters was investigated. Three catalysts were used in a radiant heater and a convective heater operated at low and high fuel consumption rates. Two of the three generally reduced CO and NO_2 emissions from the radiant heater by about 50%; the other catalyst reduced these emissions by about 25%. These same catalysts generally increased total-suspended-particulate (TSP) emissions from the radiant heater. For convective heaters, two of the catalysts slightly reduced CO emissions and slightly increased NO_2 emissions. The third catalyst slightly reduced CO emissions and increased TSP emissions during one test. Overall, the catalysts were not consistently effective in reducing pollutant emissions from kerosene heaters and in some cases increased pollutant emissions. Use of add-on catalytic devices does not appear to be an effective pollutant-control strategy for unvented kerosene heaters.

Introduction

The sales and use of portable unvented kerosene heaters have increased dramatically over the past decade. Many studies have documented the pollutant emission rates from kerosene heaters.[1-7] Carbon monoxide (CO), carbon dioxide (CO_2), nitric oxide (NO), nitrogen dioxide (NO_2), formaldehyde (HCHO), suspended particles, and semivolatile and nonvolatile organic compounds, including some nitrated and non-nitrated polycyclic aromatic hydrocarbons (PAH), can all 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 kerosene heaters. Emissions of CO, NO, NO_2, HCHO, and total suspended (TSP) particles 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 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% sulfur, and rated "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. Manufacturer's instructions were followed when installing the catalysts. Hanging wires are used to position the device slightly above the flame in a kerosene heater.

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.

A heater or heater/catalyst combination was placed on a rolling platform in a 27-m^3 environmental chamber housed in Building 44 (see Fig. 1). 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 (burn 1). The heater was left burning and was rolled out of the chamber. After 1.5 hours, the heater was rolled back into the chamber, and a second 5500 kJ of fuel was consumed (burn 2). The flame was extinguished after the second burn. The goal of this protocol was to obtain an initial and a steady-state emission rate for each test. A more-detailed description of the test protocol is reported elsewhere.[9,10]

Air-Pollution Instrumentation

Most air-pollution monitoring instrumentation was contained in the Lawrence Berkeley Laboratory's Mobile Atmospheric Research Laboratory (MARL). Figure 1 is a schematic diagram of the instrumentation in MARL and in the environmental chamber.

The MARL continuously draws samples through Teflon tubing from two locations inside Building 44 (one inside and one outside the chamber). Teflon prefilters at the inlets of the

sampling lines are changed daily to protect the sampling lines and instruments from particles. Although the MARL can only monitor gases from a single location at a given time, both lines draw continuously to minimize purge time when sampling sites are switched. The line that is not being monitored is vented to the outside via an exhaust pump. A Teflon-lined pump supplies the sample from the site being monitored to the glass mixing manifold and maintains manifold pressure at the calibration value which is slightly above atmospheric pressure. The gas analyzers draw the sample from the manifold by means of individual pumps. Only nonreactive materials (e.g., glass, teflon) are used upstream of the gas analyzers to minimize degradation of the sample.

The MARL calibration system was designed for rigorous calibration of the gas analyzers (CO, CO_2, NO, NO_2, O_2). Multipoint calibrations were performed before each series of tests, and two-point calibrations were performed daily. Certified gas mixtures diluted with "ultrapure" air using a mass-flow controlled mixing system were used to produce concentrations needed for calibration. To check for problems, such as a bad pump diaphragm or leaky lines, a gas of known concentration was injected into the inlets of the sampling lines before each test.

In addition to the instrumentation in the MARL, samplers for HCHO and TSP were also located in Building 44. HCHO was collected in refrigerated bubblers and analyzed using the modified paraosaniline method.[11] 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.[12]

Although TSP 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 (<0.6μm) particle data collected by an electrical aerosol size analyzer.[13]

Results and Discussion

Figures 2-7 summarize the pollutant emission-rate results without a catalyst (baseline condition) and with CAT1, CAT2, and CAT3 for CO, NO, NO_2, N (of NO_x = NO + NO_2), HCHO, and TSP, respectively. Statistical analysis of the emission-rate differences with and without a catalyst was deemed inappropriate because only two tests were conducted for each heater/catalyst burn-rate configuration.

It is important to note that between-test variations and the time-dependent (burn 1 compared with burn 2) variations of the pollutant emission rates were large in many cases; consequently, firm conclusions regarding the effect of the catalyst on the emission rates of all pollutants were precluded. However, several interesting trends are apparent in the data presented in Figures 2-7.

All of the catalysts reduced CO emissions, on average, when inserted into the radiant heater; however, CAT1 and CAT2 were more effective in reducing CO emissions from the radiant heater than was CAT3 (see Fig. 2). All of the catalysts slightly reduced average CO emissions from the convective heater when the heater was operated at the low burn rate; however, these reductions did not appear to be significant in view of the large test-to-test variations in the CO emission rate with the add-on catalysts. Either no change or a slight increase in CO emissions was observed from the convective heater operated at the high burn rate when the catalysts were used. Only CAT1 and CAT2 have a major consistent 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; however, NO is not considered a pollutant with major health consequences (see Fig. 3).

The emission rates of NO_2, a pollutant with more-serious health consequences than NO, were reduced by all catalysts when they were used on the radiant heater (see Fig. 4). As with CO, CAT1 and CAT2 were more effective in reducing NO_2 emissions from the radiant heater than was CAT3. All three catalysts had negligible effect on NO_2 emissions from the convective heater operated at the low burn rate, but CAT1 and CAT2 increased average NO_2 emissions from the convective heater operated at the high burn rate.

The effect of the catalysts on the N (of NO_x) emission rates were negligible for all heater/burn rate configurations except for the convective heater generated at the high burn rate (see Fig. 5). In this case, all three catalysts caused an increase in the average N(of NO_x) emission rate. Note that in all tests the average N(of NO_x) emission rate is lower during burn 2 than burn 1.

There does not appear to be a consistent affect across catalysts on HCHO emissions from the radiant heater (see Fig. 6). The use of the catalysts on the convective heater slightly increased average HCHO emissions when the heater was operated at the low burn rate and slightly decreased average HCHO emissions at the high burn rate.

TSP emission rates were the most variable of all pollutant emission rates. 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. When the convective heater was operated at the low burn rate the general effect of CAT1 and CAT3 was to increase the TSP emission rate especially during burn 2. When the convective heater was operated at the high burn rate, however, either CAT1 or CAT2 greatly reduced the TSP emission rate, whereas CAT3 caused an increase in the average TSP emission rate for burn 2.

In addition to the pollutants described in Figures 2-7, particulate sulfur emissions were measured for most tests. At least one measurement was made for each test type. 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]

Significant particulate chromium emissions were observed for all test types. Two previous studies also investigated particulate chromium emissions from kerosene heaters.[4,5] There was considerable variation in the chromium emission rate between repeat tests of the source type. 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 μg/kJ and a geometric standard deviation of 5.0.

Conclusions

Add-on catalytic devices were moderately effective in reducing CO and NO_2 emissions from a radiant heater. Two of the three catalysts reduced these emissions by roughly 50%, whereas the third reduced them by roughly 25%. However, the TSP emissions increased, in

general, with the use of a catalyst. A ten-fold increase in TSP emissions was observed in at least one test condition for all three catalysts.

For convective heaters, the add-on catalysts moderately reduced CO emissions for most test types. However, two of the three catalysts increased NO_2 emissions under two or more test conditions, and the third catalyst increased TSP emissions during one test. Average formaldehyde emissions were slightly reduced by the catalysts when the convective heater was operated at the high burn rate but were slightly increased at the low burn rate.

Overall, the add-on catalysts tested as part of this study did not consistently lower the emission rate of important pollutants; therefore, the authors cannot recommend them as an effective method for controlling pollutant emissions from unvented kerosene space heaters.

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Table I. Descriptions of Add-on Catalytic Devices.

Device Code Name	Dimensions (cm)	Catalyst Material Description
CAT1	Element is a wire mesh (2 ply) over 15-cm-diameter circular wire frame. Outer lip is 0.5 cm thick.	Wire mesh coated with platinum.
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 on 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 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. Its metal holder is a conic section 19 cm in diameter on the bottom, 15 cm on the top, and 4.5 cm thick.	Honey-combed, porous, coated ceramic.

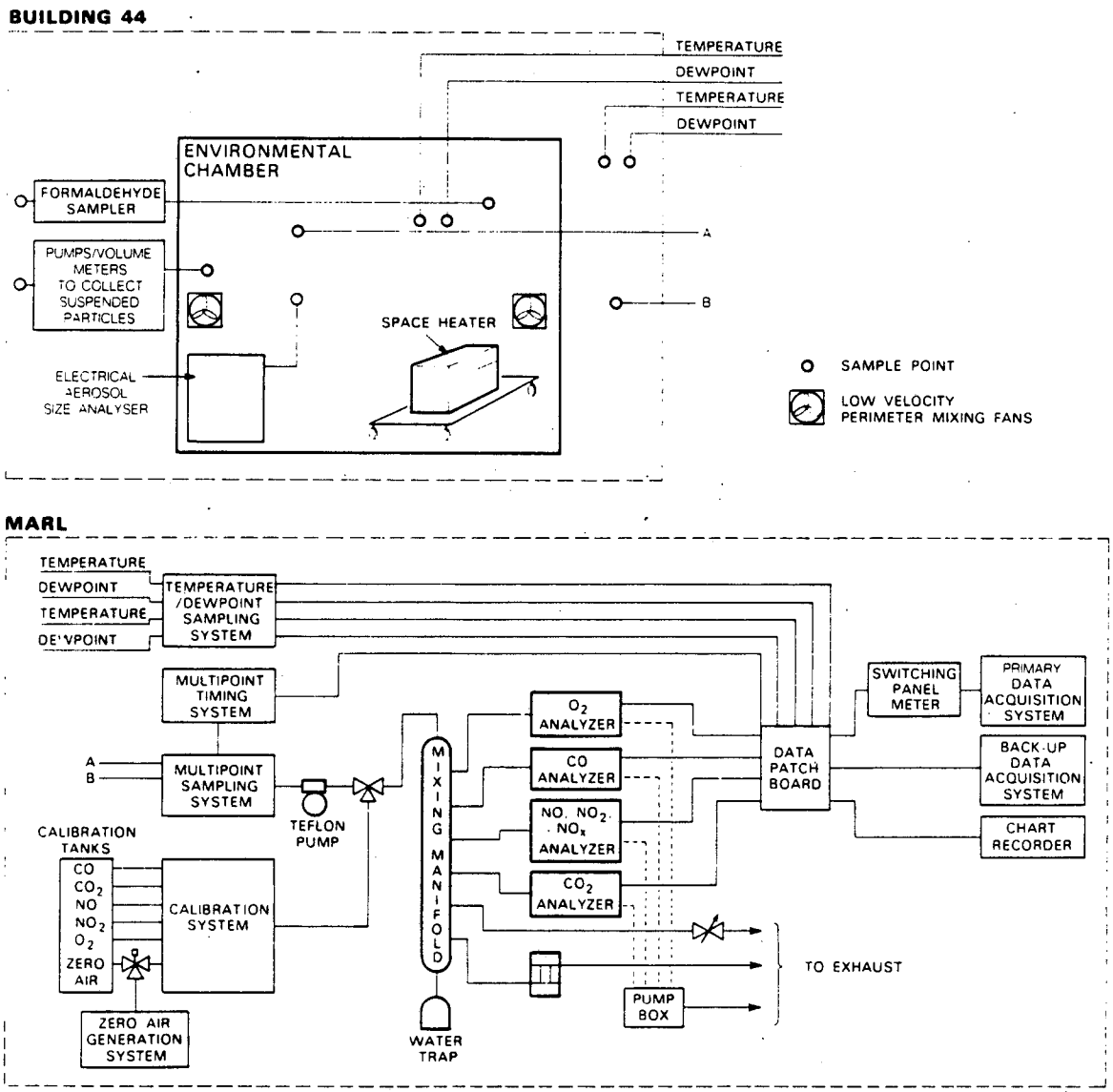

Figure 1. Schematic diagram of environmental chamber and Mobile Atmospheric Research Laboratory (MARL).

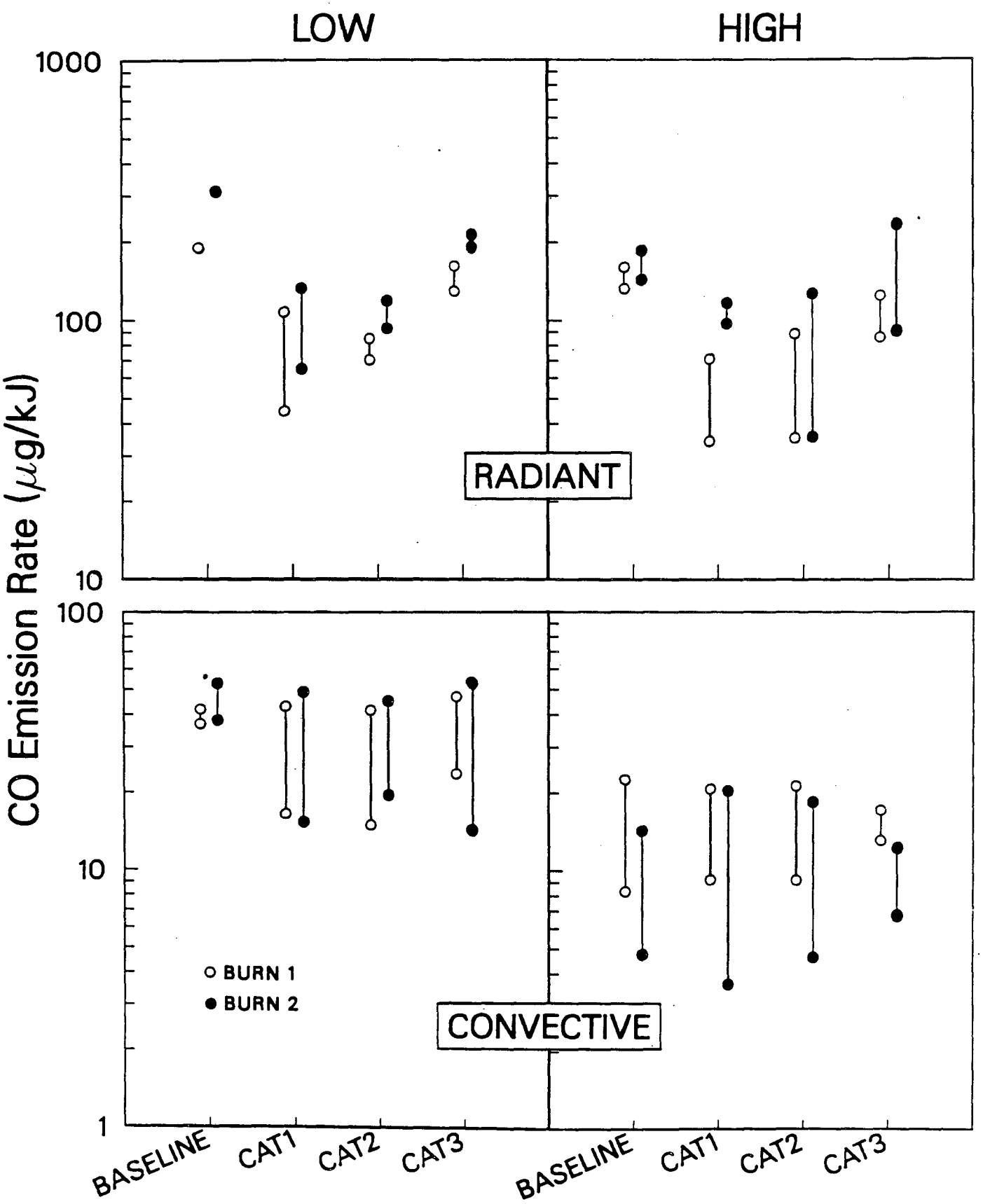

Figure 2. Initial (burn 1) and steady-state (burn 2) carbon monoxide emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

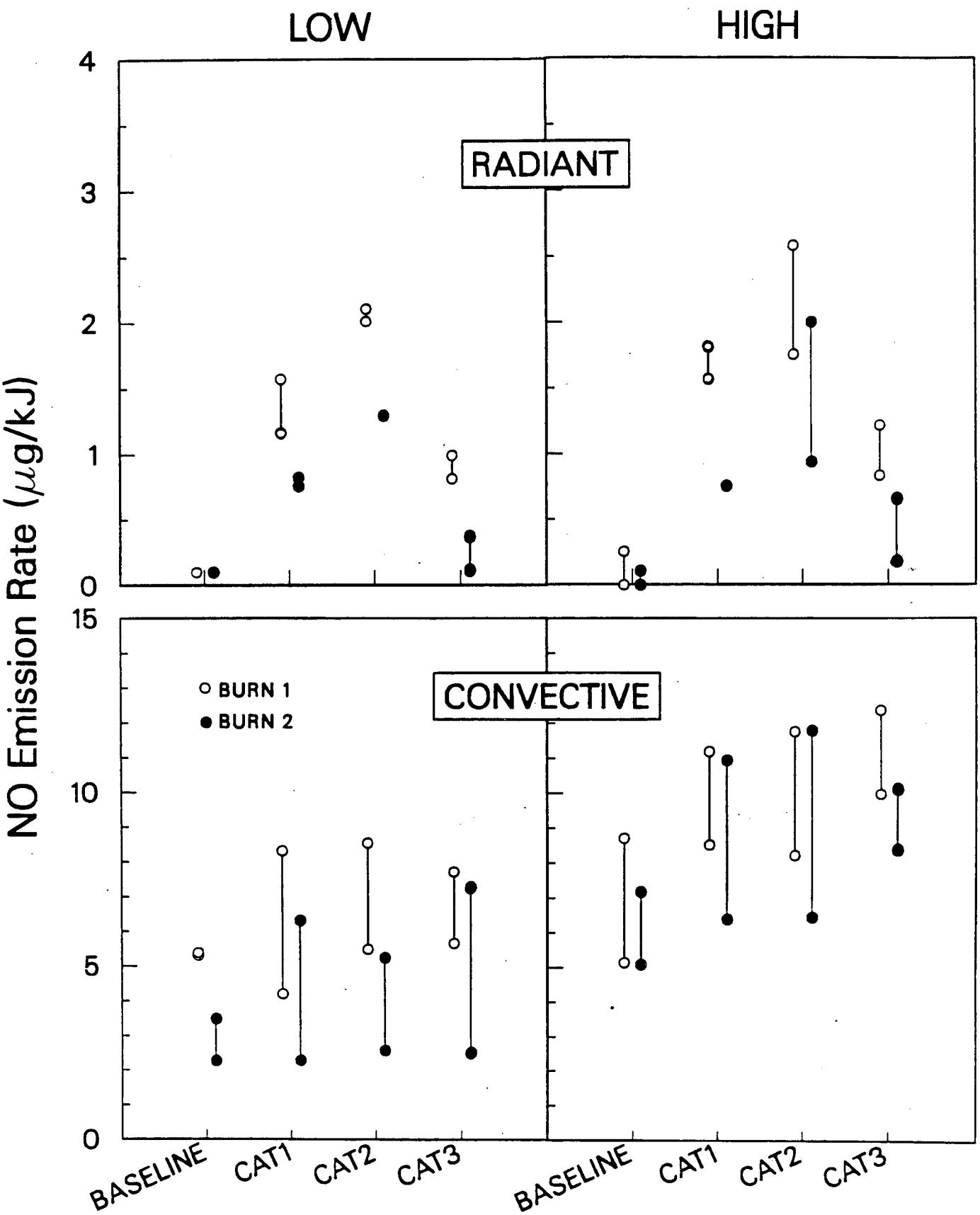

Figure 3. Initial (burn 1) and steady-state (burn 2) nitric oxide emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

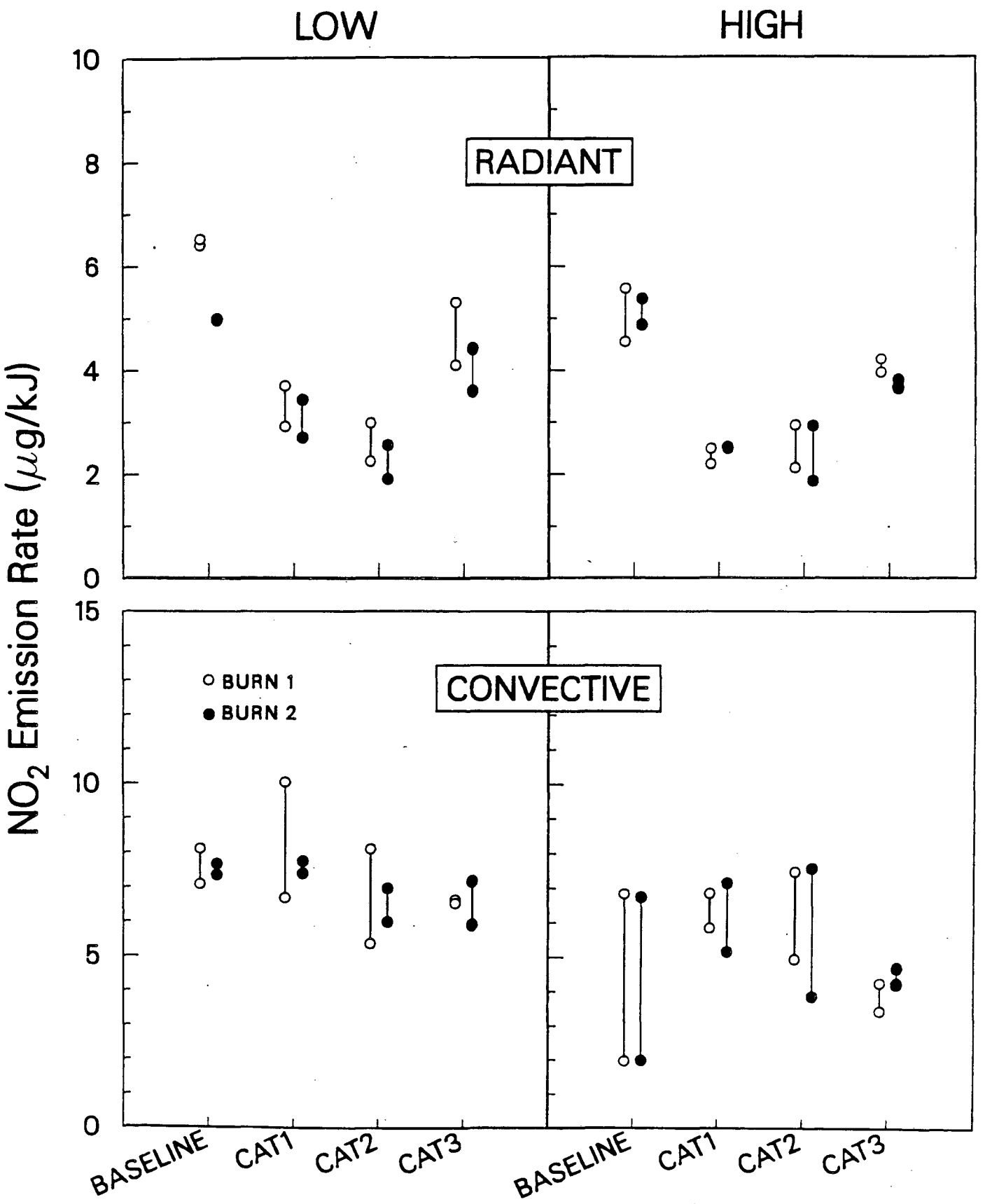

Figure 4. Initial (burn 1) and steady-state (burn 2) nitrogen dioxide emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

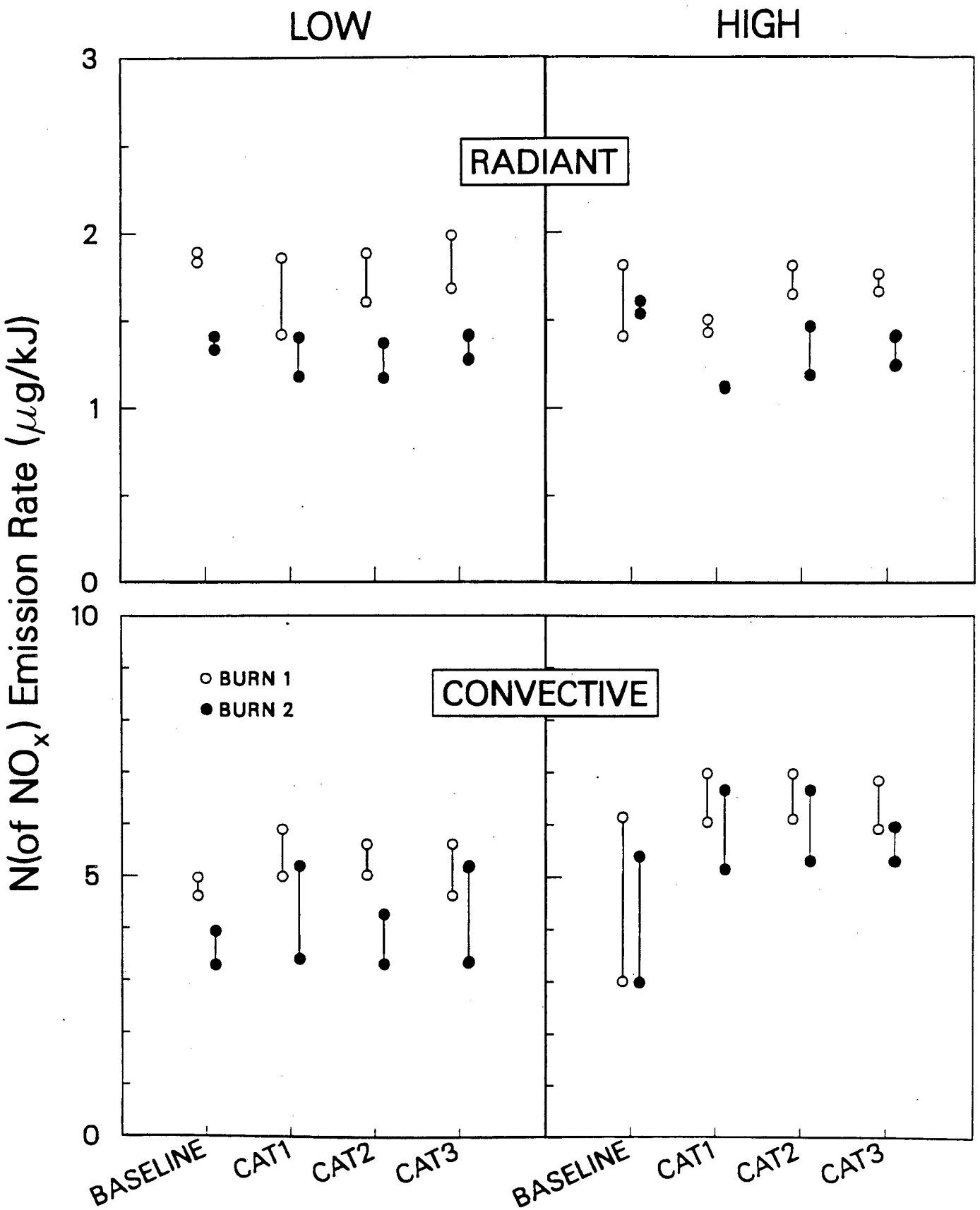

Figure 5. Initial (burn 1 and steady-state (burn 2) nitrogen oxides (as nitrogen) emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

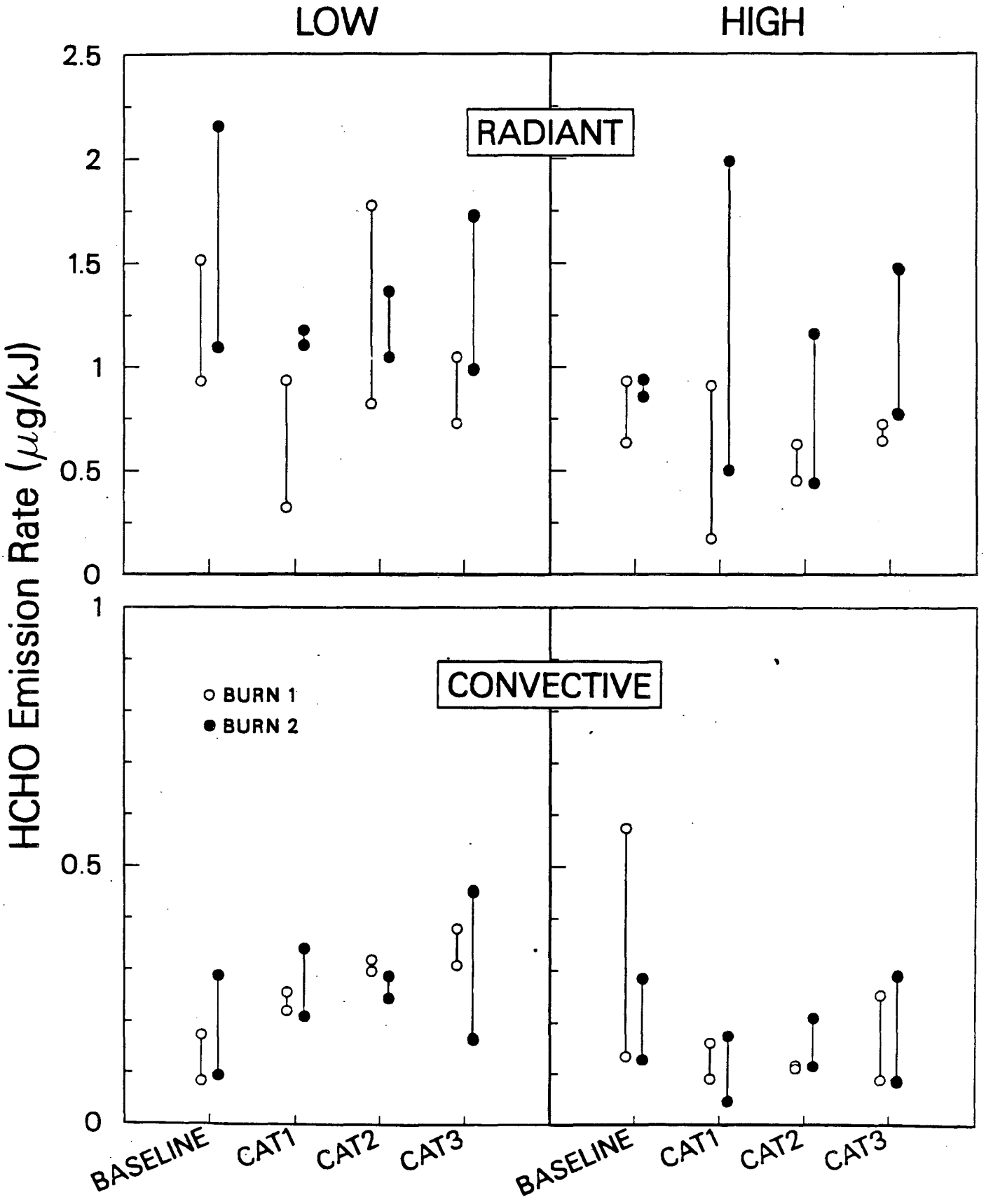

Figure 6. Initial (burn 1 and steady-state (burn 2) formaldehyde emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

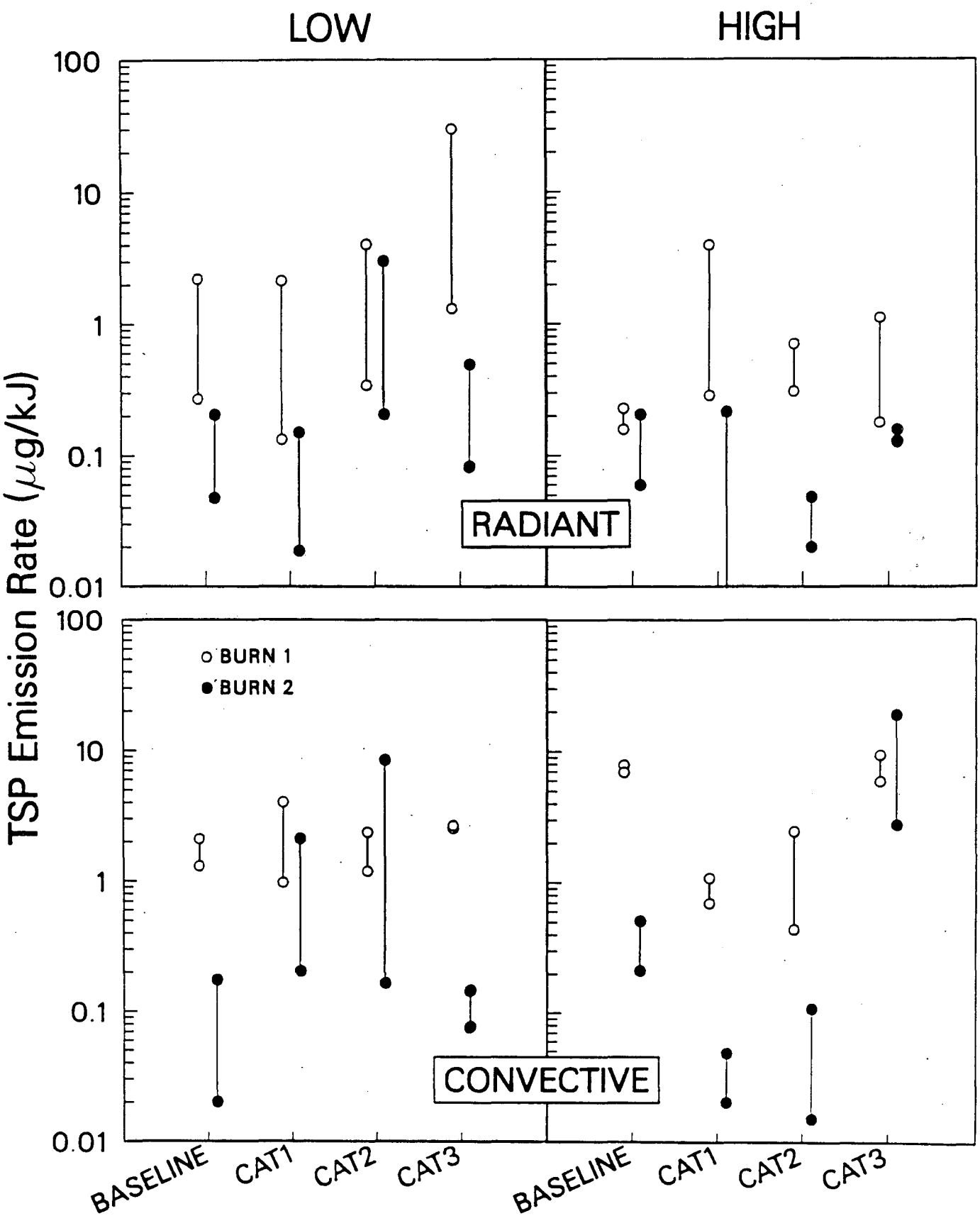

Figure 7. Initial (burn 1) and steady-state (burn 2) total suspended particle emission rates from radiant and convective kerosene heaters operated at low and high fuel consumption rates, without any catalytic device (baseline) and with CAT1, CAT2, and CAT3 add-on catalytic devices.

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