



Project Summary

Study of the Effectiveness of a Catalytic Combustion Device on a Wood Burning Appliance

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A wood stove, incorporating a catalytic combustor, was operated while burning air-dried oak at low burning rates. Gas composition was measured continuously both at the entrance and the catalyst (after the gases had left the burning wood) and at the exit of the stove (after the gases had traversed the catalyst). These continuous monitors showed a reduction of about 3:1 in volatile hydrocarbons measured by a flame ionization detector, and a comparable reduction in carbon monoxide. These monitors showed no significant corresponding reduction when the active catalyst was replaced with an identical ceramic element, but without the noble metal catalytic coating.

Grab samples collected from the flue gas early during the wood burning cycle, analyzed by MS and GC, confirmed the lower concentrations of volatile combustible species when the active catalyst was used.

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

The increased use of catalytic combustion devices on wood-burning appliances has raised a number of concerns regarding emissions from these sources into residential areas. The purpose of this study was to determine the effectiveness of catalytic combustors in reducing emissions of hydrocarbons and CO, and also to determine the

species of compounds which are emitted during the operation of a typical catalyst-equipped appliance. The stove used in this program had a honeycomb, ceramic catalytic device, referred to as a catalyst, internally within the stove.

While the catalyst is believed to be effective in promoting combustion, actual operation had not been thoroughly characterized with respect to stove operating variables. Of particular concern to this study were:

- Operating conditions where the catalyst is most effective in reducing emissions.
- Effectiveness of the catalyst in low burn-rate operation.
- Combustion products formed in the catalytic combustion process.

For this program a catalyst-equipped wood-burning appliance was tested in Battelle's combustion research laboratory. Continuous samples of the combustion gases, before and after the catalyst, were analyzed by on-line gas analyzers for O₂, CO₂, CO, THC, NO, and NO_x. Temperatures at various points in the gas stream and also within the catalyst bed were monitored during the test. A sampling train (EPA Method 5) with a packed column of XAD-2 resin was used to collect particulate and vapor-phase organics from the gas stream. A grab sample of combustion gas leaving the stove was taken for analysis of low molecular-weight species (> 100 amu) by direct mass spectrometry and selective gas chromatographic analysis.

On-line gas analyses indicate that the catalytic device is effective in reducing both total hydrocarbons (THC) and carbon monoxide (CO) at temperatures where the catalyst is active (above about 425°C (800°F)). At lower temperatures there is less effect on THC emissions. When a blank catalyst (i.e., ceramic substrate without the

noble metal coating) was used in place of the active catalyst, there was a noticeable decrease in the catalyst temperature, and the emission levels increased.

Test Methods

A test program was conducted at Battelle's Columbus combustion test facility to evaluate a catalytic-combustor-equipped, wood burning appliance. A Webster Oak stove was installed in the facility and, with the catalyst operating, the stove was conditioned for 100 hours by burning split white oak and pine. During these burns, the controls were adjusted to obtain effective burning at low wood consumption rates. Figure 1 is a schematic diagram of the stove.

Sampling Methods and Equipment

Aspirated thermocouples and rake-type sample probes in the stove sampled combustion gas both entering the catalyst (primary) and in the flue (secondary). Thermocouples monitored: (1) secondary air temperature inside the air duct within the combustion chamber, (2) several stove skin temperatures, (3) stack wall temperature, (4) sample train temperatures, and (5) ambient air temperature. Also, the viewing window over the catalyst was replaced with a fitted insert that permitted vertical traversing of the catalyst to measure temperatures within the catalyst bed. During the preliminary burns, the point of maximum temperature was determined in the catalyst and the bare thermocouple was locked at that point.

The test facility provided continuous sampling and monitoring of the stove parameters shown in Figure 2. The data collection and processing system is limited to collecting single point data. Due to limitations on data storage, most tests were designed for 110 scans at 2-minute intervals (total time, 220 minutes).

This program included six test burns. During five of the six tests, a sample for volatile gas analysis was taken at a point near the gas exit to the chimney by drawing a sample into a preevacuated 3-liter glass bulb. Also during monitoring, flue gas was sampled continuously from the stack at a point 75 cm above the flue's entrance into the insulated stack. For condensible organics, an extractive sampler (similar to an EPA Method 5 train) was used with a packed column of XAD-2 resin following the heated filter. This train includes a glass-lined sampling probe (sealed into the flue), a heated filter holder — 200°C (390°F) — with a fiberglass filter, an XAD-2 resin adsorption chamber at 20°C (68°F), a series of ice-cooled scrubbers, a drying cartridge filled with silica gel, and gas flow monitoring and gas moving devices.

Test Procedures

Tests were conducted by starting a fire in the appliance, using red oak splits. During this time, the sampling equipment was equilibrated and leak-checked, and monitoring instruments were zeroed and spanned. The data acquisition program was initiated by recording: instrument and sample codes in the data system, wood type and moisture, barometric pressure, scan interval, test duration, start time, weight and type of wood charge, and test title. Also, the sample pump and line heaters were turned on to condition the system.

After the initial wood charge had burned to glowing coals, the bed was raked flat and the electronic scale zeroed. A preweighed charge of wood was placed in the combustion chamber at exactly 1 minute prior to data acquisition with the primary setting at

"air full open." Analyzers were then checked to verify that flow rates and line pressures were within specified limits.

Upon initiation of data acquisition, the continuous sampler was started. The stove operator monitored catalyst temperature using a digital readout. When the catalyst temperature reached 425°C (800°F), the primary air supply was adjusted to a predetermined set point. This time delay was normally less than 5 minutes. At no other time during the burn was the air readjusted or fuel added to the stove. Data acquisition and extractive sampling continued until the predetermined termination time was reached.

Post-Test Procedures

After sampling was complete, the extractive sampling system was removed from the

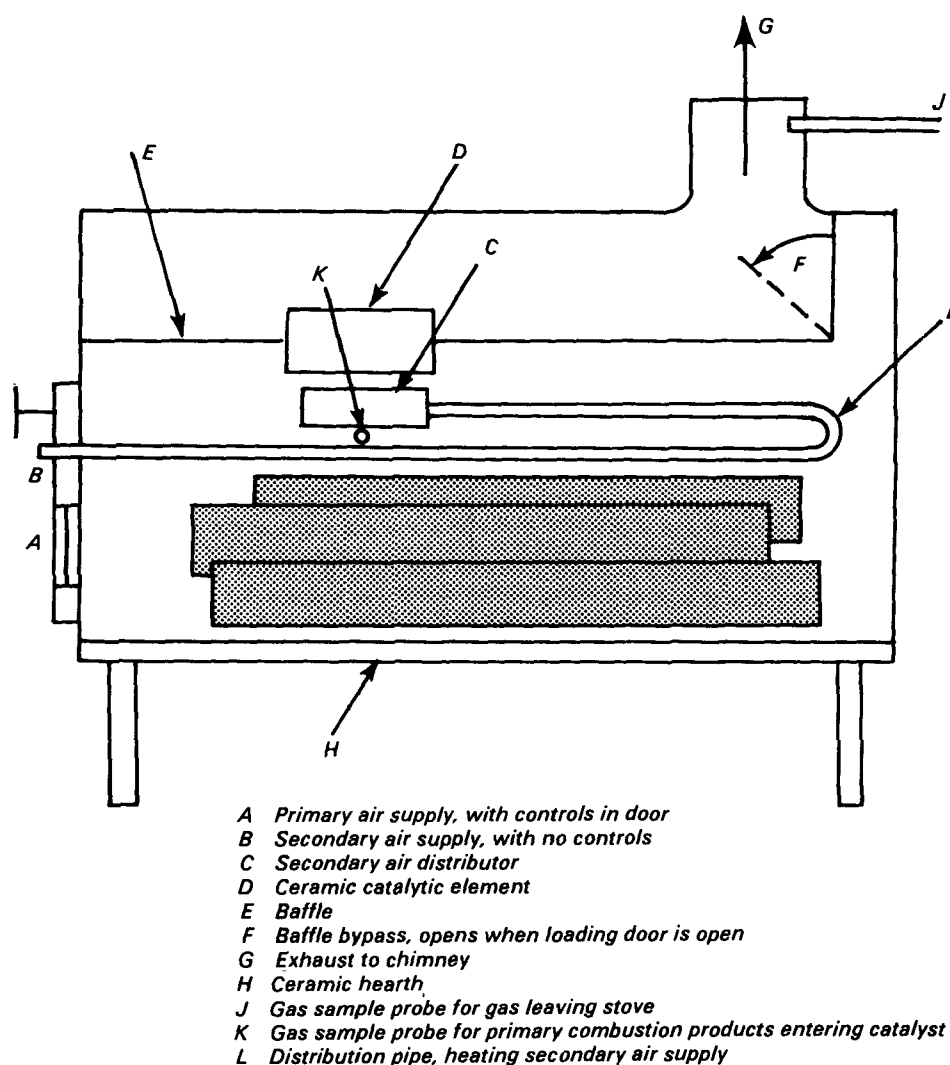


Figure 1. Schematic diagram of the catalytic stove.

stack and all openings capped with clean aluminum foil. The system was then transported to a chemistry laboratory for recovery according to the wood stove sampling protocol. Analyzers were all purged with N₂ gas and then post-test zero and span checks were made to determine instrument drift or malfunction during testing.

Test Results

The test program included six stove tests. Of these, five were run with the normal catalyst in place, and one (Test 6) was run using a ceramic substrate without the cat-

alytic coating. Tests were designed for medium to low burn rates and run as close to reproducible conditions as possible, except Test 3, which was conducted with a lower rate of primary air. All tests used four pieces of wood, together weighing about 10 lb (4.54 kg).

Continuous Sampling

Stove operating data for Tests 2 through 6 are included in Table 1. The operational data for the Modified Method 5 tests are included in Table 2. Note that Modified Method 5 tests and grab samples were taken

only on Tests 2, 3, 4, and 6. Test 5 was not sampled for organics. Continuous gas analyses were conducted at locations before and after the catalyst. The data were recorded every 2 minutes and then averaged over the entire test. The results are presented in Table 3. The first test was considered a shakedown run: reliable data were not obtained.

Emission Factors

The test results were compiled using Battelle's wood stove data reduction program. These results were then presented graphically using a Techtronix Plot 50 program. The emission factors for CO and THC as grams per kilogram of wood burned are shown in Figures 3, 4, and 5. These presentations show the effect of secondary combustion in the catalyst on CO and THC emissions.

Grab Sample Results

The composition of volatile gases is summarized in Table 4. Test 6, made with a blank catalyst, clearly shows the effect of the catalyst during Tests 1 through 4. Without the catalyst, higher concentrations of CO, THC, and H₂ were found. Also elevated benzene levels were found in the blank run. Benzene and ethanol are not gases at room temperature and atmospheric pressure; therefore, these data are approximates — true concentrations may be much higher. All results are reported on a dry basis.

Discussion of Test Results

Wood combustion is generally characterized by initially fast surface combustion in which moisture and organic pyrolysis products are evolved, during which an outer char layer is formed. During the middle portion of typical wood burning, pyrolysis products are evolved. Slow burning takes place in this portion of the burn, with pyrolysis products and interior moisture passing through the char layer simultaneously. Late in a typical burn, residual fuel is essentially all char; therefore, hydrocarbon emissions are very low and surface burning takes place. The organic emissions, which are products of incomplete combustion, generally are more concentrated during the early portion of a test burn.

These effects are observed by examining the emission factors shown in Figures 3, 4, and 5. Pyrolysis products, shown by THC emissions, usually have initially high values early in the test and lower values as the wood becomes charred. Irregularities are presumably associated with shifting wood and inherent irregularities within the pieces of wood.

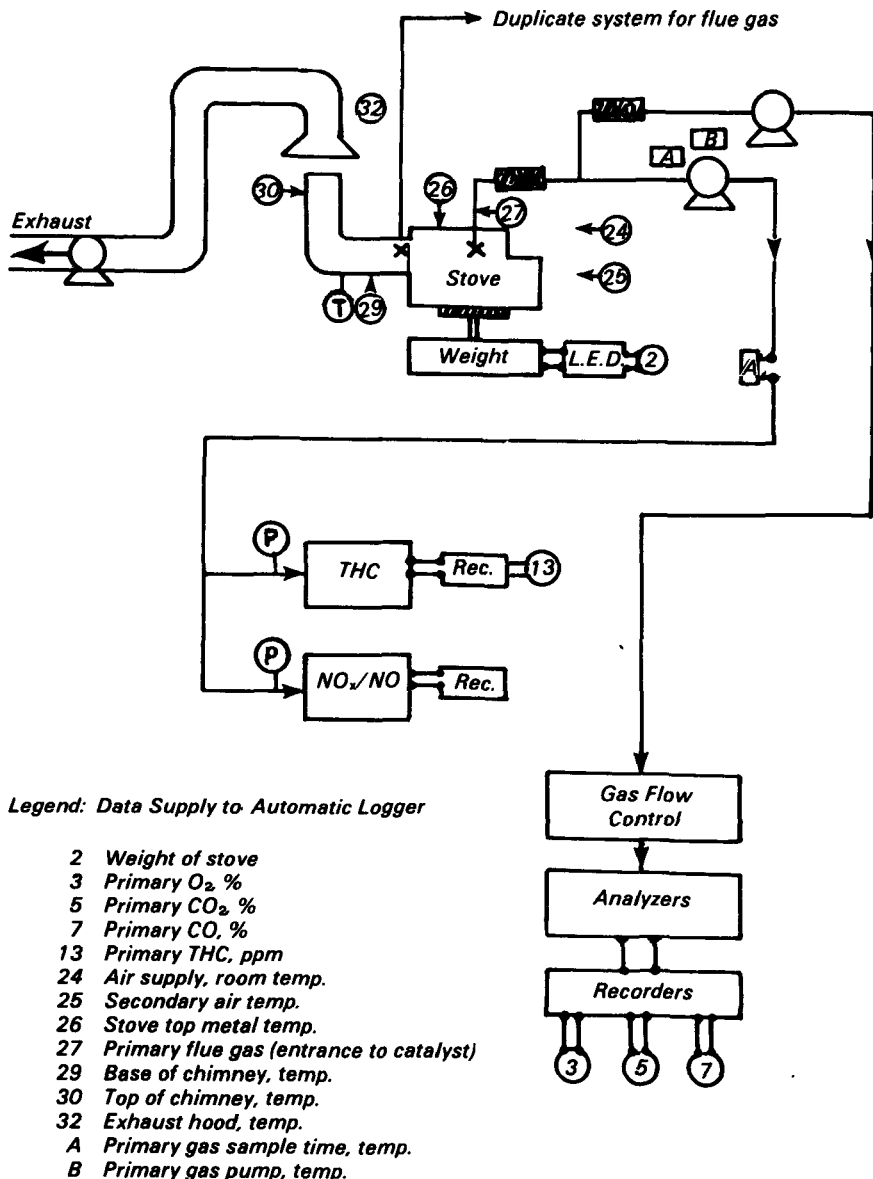


Figure 2. Schematic diagram of sampling system.

Table 1. Operating Conditions for Stove Tests

Test No.	Weight of Wood		Average (actual) Burn Rate		Average Catalyst Temp.		Average Stack Temp.		Condition
	lb	kg	lb/hr	kg/hr	°F	°C	°F	°C	
2	10.0	4.5	3.5	1.6	941	505	364	184	High air
3	9.4	4.3	2.4	1.1	775	413	343	173	Low air
4	10.4	4.7	2.6	1.2	919	493	376	191	Med. air
5	10.4	4.7	2.3	1.0	898	418	349	176	Med. air
6	10.2	4.6	2.1	1.0	676	358	318	154	Uncoated catalyst

Table 2. Results of Modified Method 5 Samples

Test No.	Volume Sampled		Sample Time min.	Flue Gas Moisture percent H ₂ O	Average Filter Temp.		Particulate Emissions ^a	
	dscf	dscm			°F	°C	gr/dscf	g/dscm
2	99.85	2.83	135	6.7	407	208	0.0130	0.0298
3	109.17	3.08	191	6.0	405	207	0.0256	0.0586
4	131.15	3.71	310	4.9	410	210	0.0268	0.0613
6	120.53	3.41	219	3.3	406	208	0.0186	0.0426

^aCorrected to 12 percent CO₂.

Table 3. Average Flue Gas Analysis

Test No.	O ₂ , percent		CO ₂ , percent		CO, percent		THC, ppm		PAH, mg/m ³
	Primary	Secondary	Primary	Secondary	Primary	Secondary	Primary	Secondary	Secondary
2	11.2	17.4 ^a	9.0	3.0 ^a	0.9	0.1 ^a	4320	1135 ^a	3.4 ^a
3	13.4	—	6.7	—	—	—	2922	1001	3.4
4	12.7	17.3	7.6	3.4	0.7	0.1	5089	2184	2.0
5	13.8	15.8	7.2	5.0	0.7	0.2	4029	1279	—
6	12.1	16.3	8.1	4.2	0.8	0.5	3550	3186	3.2

^aAveraged only over last 105 minutes of test run. Early secondary readings not valid during Test 2

Table 4. Volatile Flue Gas Composition

Test No.	Volume Percent (Dry Basis)					Instrumental Reproducibility
	1	2	3	4	6	
Nitrogen	77.3	77.2	77.4	77.5	76.5	± 0.2
Oxygen	14.1	8.85	13.8	12.0	10.1	± 0.1
Carbon dioxide	7.11	12.5	7.46	9.17	10.1	± 0.05
Carbon monoxide	0.35	0.38	0.20	0.25	1.30	± 0.03
Argon	0.94	0.94	0.94	0.95	0.94	± 0.02
Methane	0.13	0.09	0.15	0.07	0.16	± 0.03
Ethanol ^a	0.03	0.01	0.01	0.01	0.03	± 0.01
Hydrogen	0.05	0.05	0.05	0.05	0.15	± 0.05
Benzene	0.01	0.01	0.01	0.01	0.02	
	Parts Per Million By Volume					
Ethylene or acetylene	200	214	175	149	732	± 10
Ethane	115	50	100	51	117	± 10
Propylene	20	18	22	14	45	± 5
Propane	17	0.2	12	4	45	± 1
Unknown No. 1 ^b	2	18	13	1	4	
Unknown No. 2	2	1	1	1	2	
Unknown No. 3	45	20	25	17	39	
<i>l</i> -Butene	11	1	1	1	9	± 2
<i>n</i> -Butane	1	1	1	1	1	
Hydrogen sulfide	0.5	0.5	0.5	0.5	0.5	
Carbonyl sulfide	0.5	0.5	0.5	0.5	0.5	
Carbon disulfide	0.5	0.5	0.5	0.5	0.5	
Sulfur dioxide	1	1	1	1	1	

^aPrimarily ethanol.

^bCalculations based on normal sensitivity.

Effect of Stove Operation on Combustion

A wood heating appliance is generally operated at a fixed rate of combustion air, although thermostatically controlled air dampers are available. Decreasing pyrolysis and combustion rates during the burn cycle results in: (1) increasing excess air levels, and (2) decreasing combustion gas temperatures. These are compound effects since increased excess air thermally dilutes the combustion gas temperature. This effect can be observed in Figure 5 where excess air and combustion gas temperatures are plotted relative to time.

Catalyst Performance

With a catalytic converter in the stove, the catalyst bed heats up very quickly: as it reaches about 260°C (500°F), the catalytic action becomes effective and secondary combustion starts. Even when the gas temperature entering the catalyst goes slightly below 260°C (500°F), the catalyst is still effective and maintains ignition with at least partial burning of the combustible material. Figure 6 shows a typical test with peak temperatures for gas leaving the burning wood at about 315°C (600°F) as they enter the catalyst. This temperature falls off throughout the remainder of the burn, reaching a temperature just above 175°C (350°F) at the end of the test burn. This, referred to as the primary gas flow, is subsequently mixed with heated secondary air upon entering the catalyst. Figure 7 shows the typical catalyst temperature over a burn cycle. These temperatures rise after heated air is added to the primary combustion products, and secondary combustion begins. This temperature goes much higher and stays high throughout about two thirds of the test period, indicating active catalytic combustion.

When the catalyst was replaced by an identical ceramic substrate that had not been coated with the catalyst, the early temperatures were slightly lower and the blank catalyst temperature dropped to a lower value late in the test run. Figure 7 shows the differences dramatically: the upper curve is with the activated catalyst, and the lower curve is with the blank catalyst.

Effect of Catalytic Action on THC and CO Emissions

Secondary combustion by catalytic activation of combustion products can be initiated at temperatures around 260°C (500°F). The measured effect on emissions is a reduction in THC and CO levels measured before and after the catalyst. Figure 8 shows the effect of the catalytic action on hydrocarbon emissions. Emissions are reported in pounds of total hydrocarbons per thousand pounds of

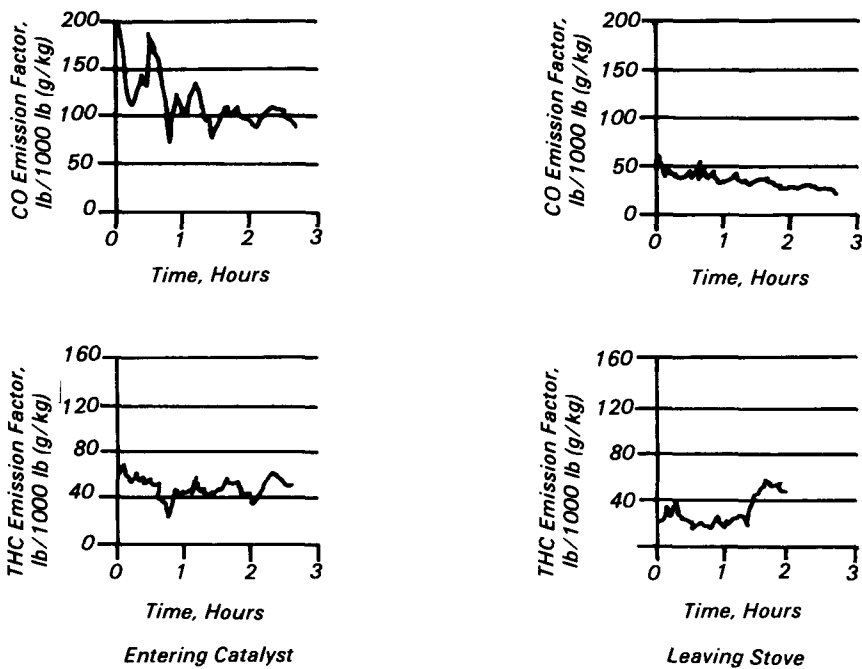


Figure 3. Emission factors with active catalyst —Test 4.

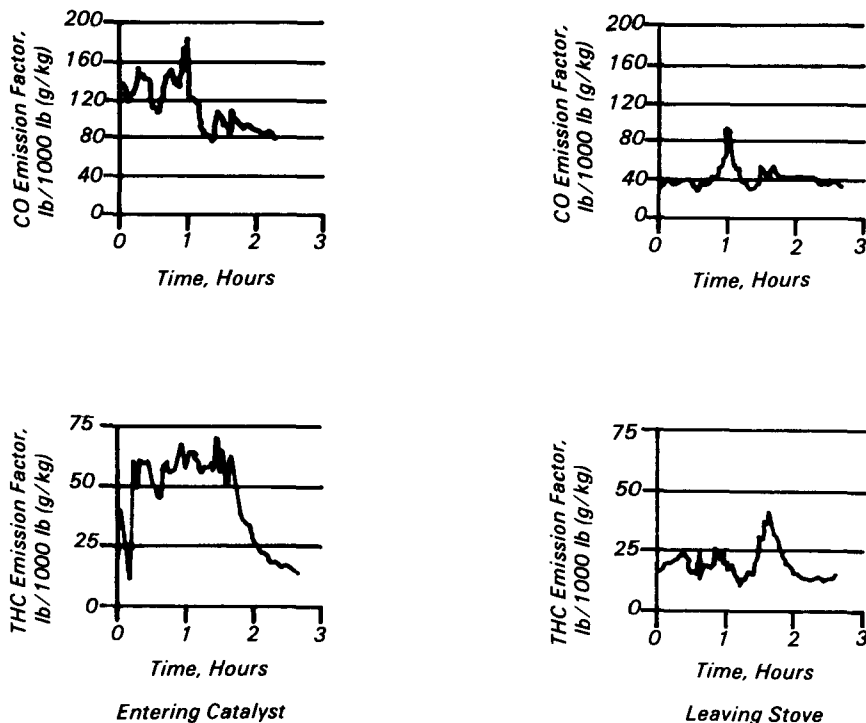


Figure 4. Emission factors with active catalyst —Test 5.

wood burned. Therefore, the hydrocarbon concentrations going into the catalyst (shown by the upper curve) and the hydrocarbon emissions leaving the stove (shown by the lower curve) are normalized to the same reporting units. There is a significant reduction in hydrocarbon emissions through two-thirds of the burn period using an active catalyst. After that period, presumably the wood has been reduced to char, and burning after that point has low hydrocarbon emissions. These data correspond to hydrocarbons with boiling points less than about 177°C (350°F). Total hydrocarbon data are measured in the FID as methane equivalents and are not absolutely quantitative. They do represent valid comparative values for evaluating catalyst performance.

CO emissions are also effectively reduced by catalytically initiated combustion. In most cases, CO emissions downstream of the catalyst were 30 to 50 percent of the emissions entering the catalyst (Figures 3 and 4). Neither CO nor THC emissions were significantly reduced in the one test which used an inactive catalyst (Figure 5).

In examining the effectiveness of the catalyst in reducing CO and THC, two combustion processes must be considered: (1) the catalytic surface reactions which are diffusion-limited (for hydrocarbons the assumed reaction is directly to CO₂ and H₂O without formation of CO); and (2) the gas-phase reactions which are kinetically limited and are assumed to react by oxidation to CO, H₂O, and H₂, followed by downstream conversion to CO₂ and H₂O. Therefore, the existence of CO in the catalyst outlet is evidence of gas-phase reactions. In a catalyst-equipped appliance, the suspected reaction is surface catalysis of hydrocarbons and gas-phase reaction of CO emissions. An unknown effect in wood combustion is the action of the catalyst on hydrocarbons with oxygen-containing substituents; e.g., aldehydes, ketones, phenolic groups, and hydroxy groups. For most oxygenated compounds, bond energies would indicate that the CO group would be eliminated and then oxidized to CO₂ by gas-phase reactions.

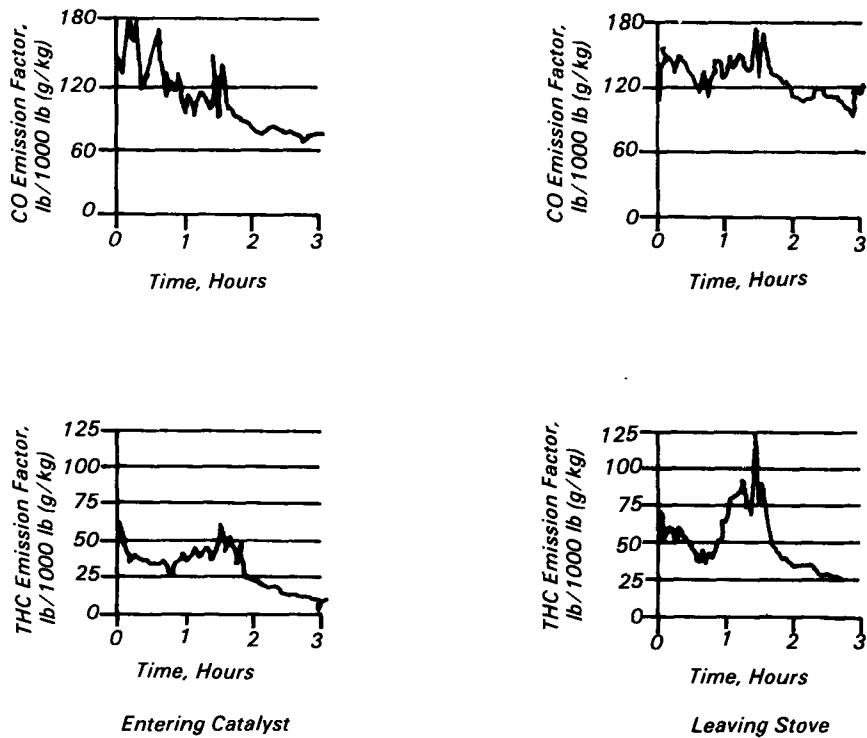


Figure 5. Emission factors with inactive catalyst—Test 6.

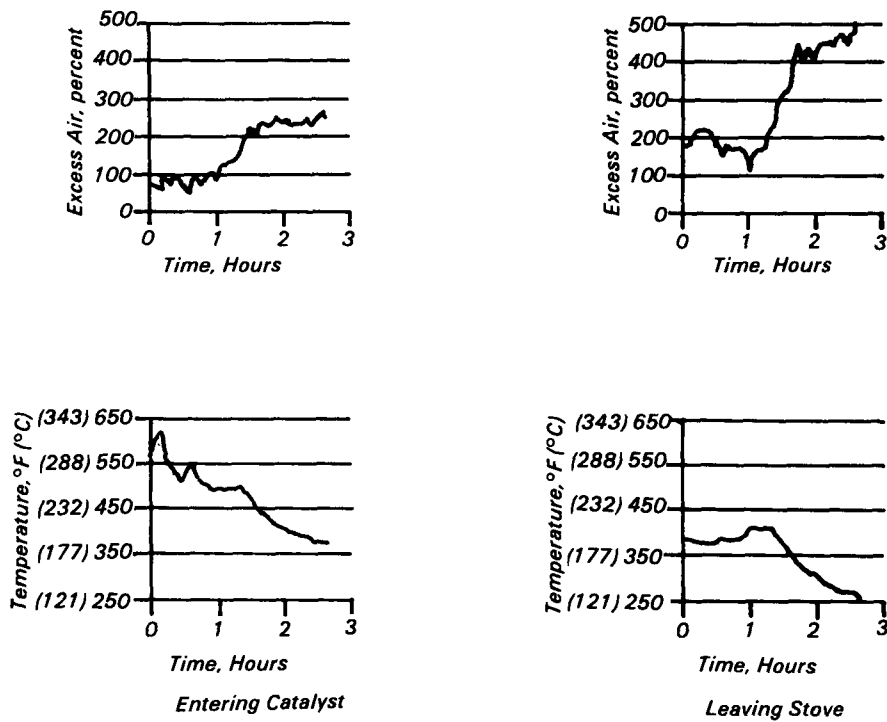


Figure 6. Excess air and flue gas temperatures with active catalyst —Test 5.

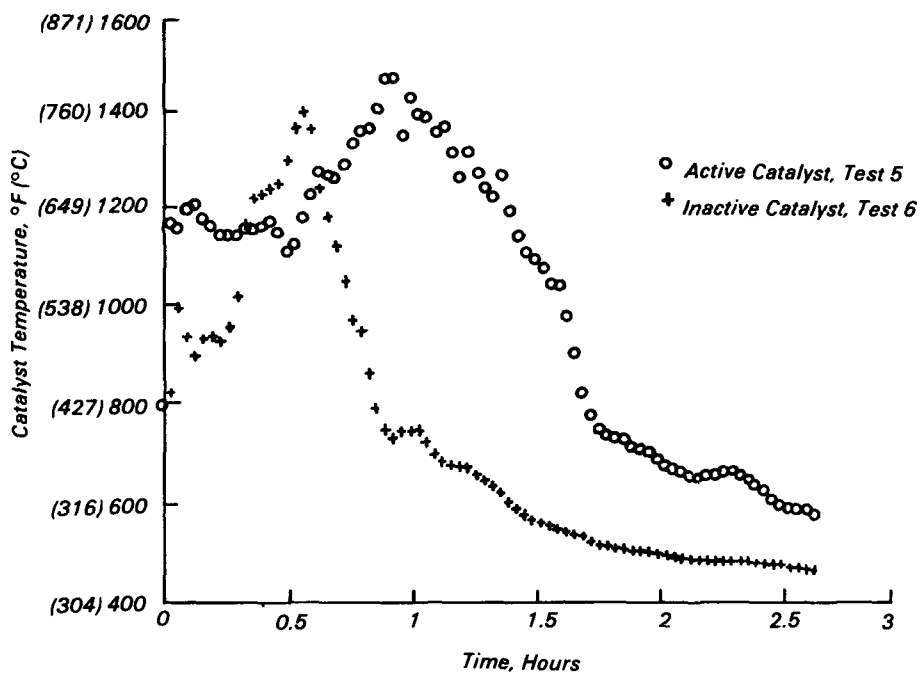


Figure 7. Temperatures within catalyst.

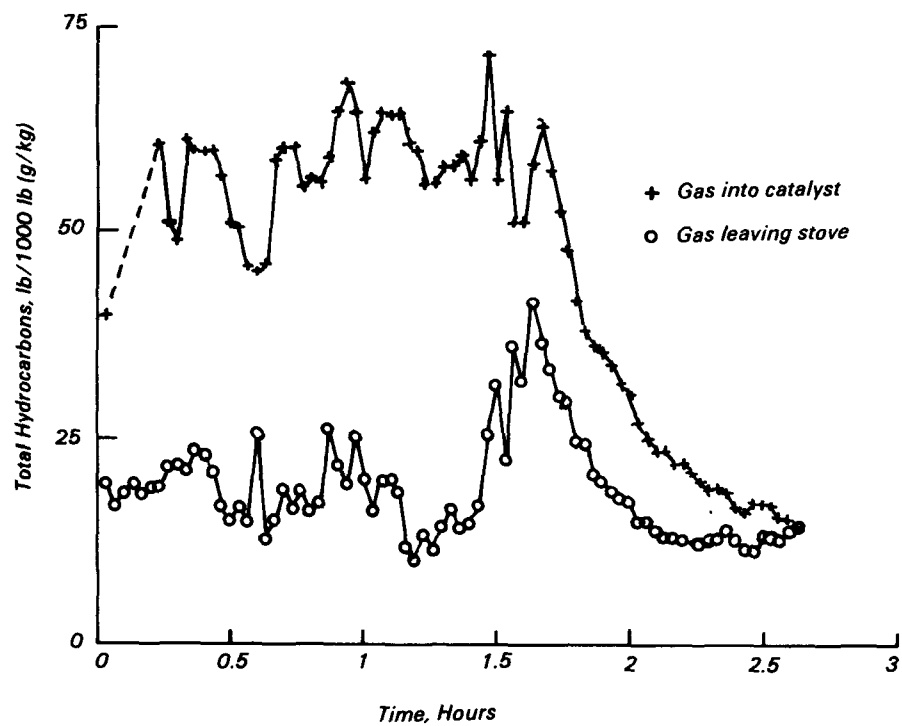


Figure 8. Hydrocarbon emission rates with active catalyst — Test 5.

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Michael C. Osborne is the EPA Project Officer (see below).

The complete report, entitled "Study of the Effectiveness of a Catalytic Combustion Device on a Wood Burning Appliance," (Order No. PB 84-171 545;

Cost: \$8.50, subject to change) will be available only from:

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