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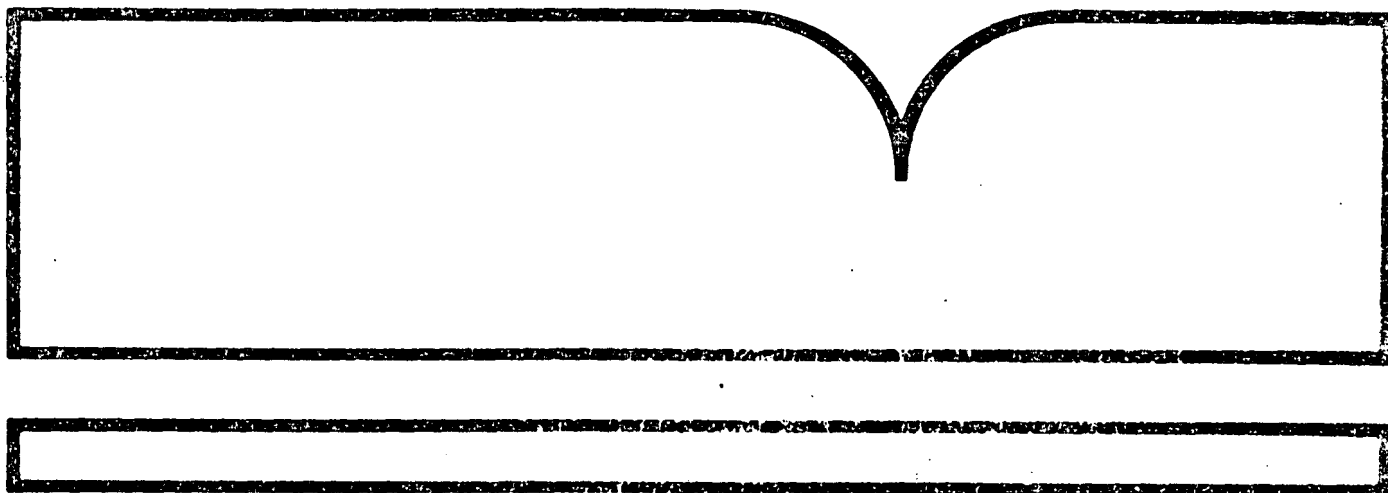
Combustor Study of the Deactivation of a  
Three-Way Catalyst by Lead and Manganese

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COMBUSTOR STUDY OF THE DEACTIVATION OF A  
THREE-WAY CATALYST BY LEAD AND MANGANESE

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## ABSTRACT

The activity and durability of a platinum-rhodium automotive three-way catalyst were investigated as a function of lead and manganese fuel levels using a pulse-flame combustor. Total hydrocarbons, carbon monoxide, and nitric oxide conversions and three-way (HC/CO/NO) conversion efficiency windows were determined for approximately 24,000 combustor-simulated miles. The window for 80% HC/CO/NO efficiency disappeared at approximately 9,000 miles, 13,500 miles, and 4,500 miles for 0.5 g of lead per gallon of fuel, 0.0625 g of manganese per gallon of fuel, and a combined manganese and lead misfueling study, respectively. The catalyst's nitric oxide reduction activity displayed the greatest sensitivity to catalytic poisoning with both lead and manganese fuels.

THE WIDESPREAD USE OF CATALYTIC CONVERTERS on automobiles and the subsequent need for a laboratory method that permits realistic screening of these catalysts prompted the development of the pulse-flame combustor (1,2).\* The combustor used in this study was developed by Amoco Oil Company under contractual agreement with the U.S. Environmental Protection Agency (EPA) (3). The apparatus was subsequently modified by the Mobile Source Emissions Research Branch of EPA. The output of the combustor closely resembles engine exhaust with respect to gaseous composition, contaminants, and space velocity. The durability of a three-way monolithic catalyst was evaluated by exposure to simulated auto exhaust. Catalyst activity was measured as a result of poisoning with antiknock additives. Poisoning of the platinum/rhodium (Pt/Rh) catalyst by fuels containing low concentrations of manganese (Mn) in the form of methylcyclopentadienyl manganese tricarbonyl (MMT) (4-8) and lead (Pb) in the form of tetraethyl lead (TEL) (9-12) was studied with this combustor.

The three-way catalyst (TWC) emission control system controls exhaust levels of the three regulated automotive pollutants: unburned hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NO<sub>x</sub>). This system controls the exhaust levels by simultaneously oxidizing unburned HC and CO to carbon dioxide (CO<sub>2</sub>) and water (H<sub>2</sub>O) and by reducing nitric oxide (NO) to nitrogen (N<sub>2</sub>). The TWC works properly in a narrow "window" of exhaust gas composition. The exact composition is achieved only when the engine (or combustor) gets the ideal (stoichiometric) mixture of air and fuel, a 14.7:1 ratio. For example, a TWC conversion efficiency profile, depicted in Figure 1, indicates that the 80% conversion efficiency window for the three pollutants of interest (HC, CO, and NO) occurs in a specific region of air/fuel ratio(s) (see shaded area), or redox potential. The redox potential (R) is the measure of the gas mixture stoichiometry of reducing components to oxidizing components. Therefore, at  $R = 1$ , a stoichiometric gas mixture is present. In the lean region ( $R < 1$ ), oxidation is favored, and the NO conversion efficiency is reduced. In the rich region ( $R > 1$ ), reduction is favored, and the HC and CO conversion efficiencies are reduced. Therefore, for the TWC to act properly, the exhaust gas composition must be in the 80% conversion window. If the gas mixture is not in this range, excess HC, CO, or NO<sub>x</sub> emissions will result. Even when the proper exhaust gas composition is reaching the catalyst, excess emissions may result because of damage (e.g., thermal sintering) or poisoning of the active oxidation and/or reduction sites on the catalyst.

## EXPERIMENTAL

APPARATUS - A pulse-flame combustor was used to study the poisoning of a commercially available Pt/Rh TWC by Pb and Mn derived from TEL and MMT antiknock additives, respectively. The combustor consisted of a fuel delivery

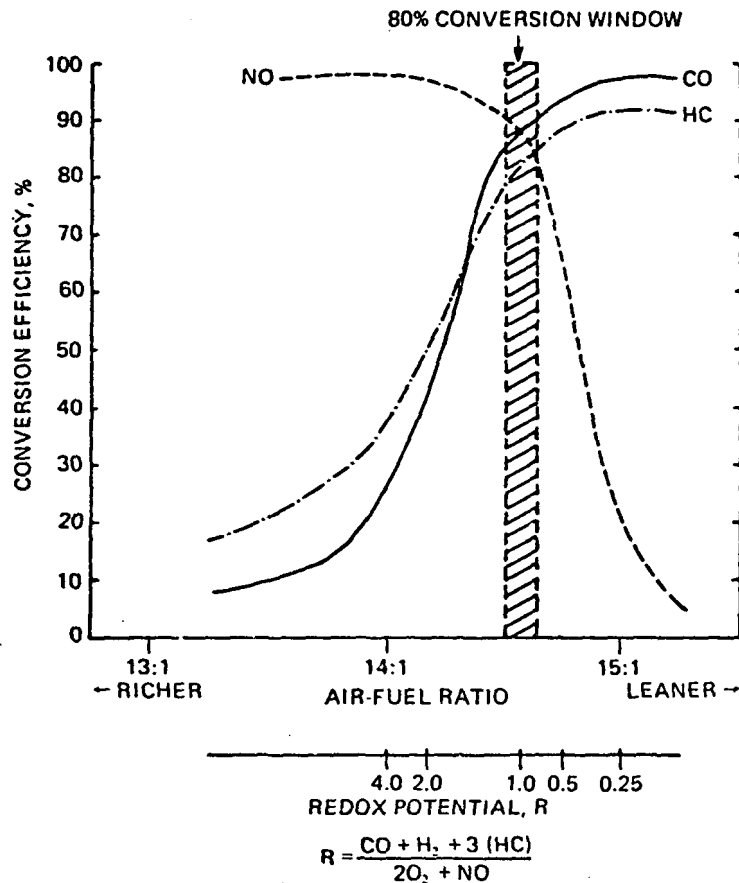


Fig. 1 - Three-way catalyst efficiency profile

system that incorporated primary and auxiliary fuel cells, a carburetor and mixer assembly, an ignition furnace, and a controlled-temperature catalyst furnace (Figure 2).

The primary fuel cell used electrolysis of a saturated barium hydroxide solution to deliver fuel to the combustor carburetor. A 90-volt potential applied across two electrodes immersed in the electrolyte solution caused hydrogen ( $\text{H}_2$ ) and oxygen ( $\text{O}_2$ ) to be released at a constant rate. These gases were forced into the water cell, where they displaced water into the fuel cell. The water then displaced the fuel at a rate that was directly proportional to the current flowing through the electrolyte cell, thereby delivering fuel to the carburetor at a constant rate. The Pyrex<sup>®</sup> glass carburetor, which was heated to 60°C, vaporized the liquid fuel and mixed it with  $\text{N}_2$  for delivery to the mixer. Three bubbles were blown into the main body of the carburetor to provide better mixing and to allow for expansion of the fuel vapors. The mixer assembly blended the fuel vapor/ $\text{N}_2$  mixture with  $\text{O}_2$  before combustion. The mixer assembly also housed a flame adjuster that quenched the flame at the mixer tip after ignition.

The fuel delivery system for the auxiliary (additive) fuel was used only during the catalyst aging mode to supply nonvolatile fuel additives to the flame. The auxiliary fuel system was similar in design to the primary fuel delivery system. The fuel from the auxiliary fuel cell was delivered to an ultrasonic atomizer where it was dispersed directly into the carburetor tube as a very fine mist. When the combustor was used in the aging mode, the primary fuel was delivered to the carburetor at a flow rate of 0.102 ml/min. Fuel additives, such as TEL or MMT, were added to the iso-octane in the auxiliary fuel cell and delivered via the ultrasonic atomizer into the combustion tube at a rate of 0.034 ml/min. The total fuel flow entering the combustion furnace (i.e., the primary flow at 0.102 ml/min and the auxiliary flow at 0.034 ml/min) was 0.136 ml/min. Combustion of this fuel resulted in an exhaust gas flow rate of approximately 750  $\text{cm}^3/\text{min}$ . During the aging mode, all of the exhaust gases were allowed to flow across the catalyst at a space velocity of approximately 90,000  $\text{h}^{-1}$ .

When the combustor was used to evaluate catalyst activity (shown by dotted lines in

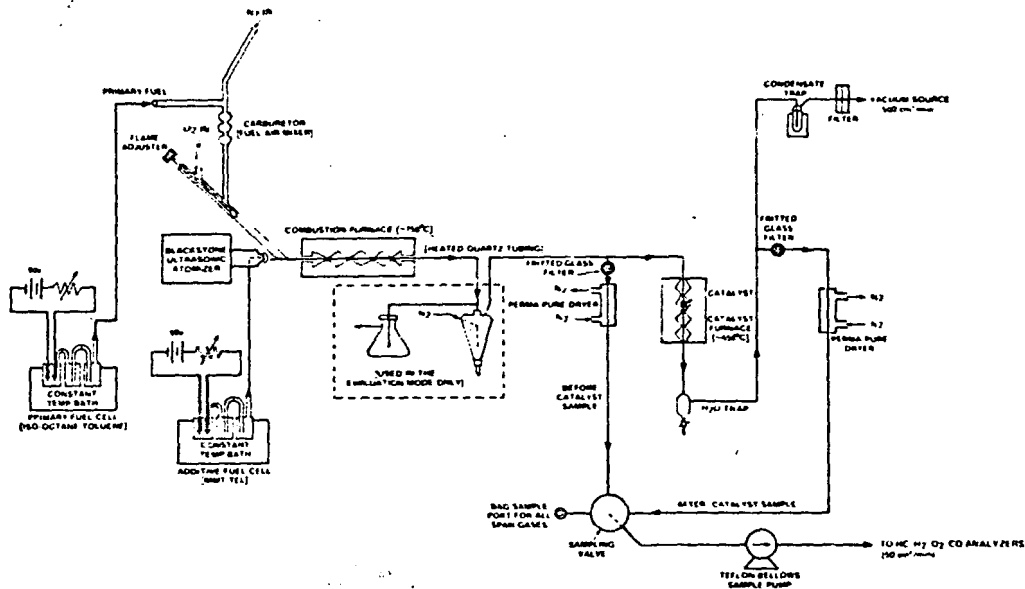


Fig. 2 - Pulse-flame combustor schematic

Figure 2), only 500 cm<sup>3</sup>/min of the combustion exhaust gases were allowed to flow through the catalyst at a space velocity of about 60,000 h<sup>-1</sup>, and the remainder of the exhaust gas was vented to the atmosphere. During the evaluation mode, a separatory funnel was provided between the combustion tube and the catalyst tube to function as a water trap and to allow thorough mixing of the combustion exhaust gases with dilutive N<sub>2</sub>. Exhaust gases from the combustor were pulled through Perma-Pure<sup>®</sup> dryers by a Teflon<sup>®</sup> bellows sample pump to reduce their moisture content, thereby reducing the chance of condensation (13). A five-way stainless steel ball valve allowed selection of the sample to be analyzed and provided delivery of calibration gases to the analytical instrumentation.

**ANALYTICAL SCHEME** - The exhaust gas sampling system (Figure 3) was configured to provide both real-time and sample loop measurements of the exhaust gas. The exhaust gas was delivered by a Teflon bellows pump to a Monitor Labs Model 8430H NO/NO<sub>x</sub> analyzer and a Perkin-Elmer 3920 gas chromatograph. The NO sample flow was regulated with a flow controller and delivered to a diluter to be diluted to a 10:1 mixture. The chemiluminescence detector and 10:1 diluter permitted real time determination of NO at a minimum detection limit of 1 ppm. Total HC were determined by a flame ionization detector (FID). The FID inlet was connected to the outlet of the sample pump manifold and a constant 15 cm<sup>3</sup>/min flow was maintained with a digital flow controller. The constant flow rate sample permitted accurate determination of total HC at the 2 ppm detection limit.

Gas chromatography with thermal conductivity detection was used to determine H<sub>2</sub>, O<sub>2</sub>, and CO levels. The chromatographic column was 6 ft x 1/8 in. stainless steel packed with 60/80 mesh 13X molecular sieve. The column oven was maintained at 60°C and was programmed to reach 90°C in 10 min; the helium carrier gas flow rate was maintained at 20 cm<sup>3</sup>/min through the column. The 1-cm<sup>3</sup> sample loop permitted accurate determinations of 0.1% H<sub>2</sub>, 0.05% O<sub>2</sub>, and 0.05% CO.

**CATALYST DEACTIVATION STUDIES** - The pulse-flame combustor was used to study the deactivation of a commercially available TWC for 1980 vehicles. Test conditions are summarized in Table 1. The neat fuel used in the studies contained 70% iso-octane, 30% toluene, and 0.025% sulfur. Study A aged the catalyst with neat fuel alone, thereby simulating approximately 22,500 miles of vehicle operation. Evaluation of the catalyst activity was performed using only neat fuel (studies A, B, C, and D). Study B aged the catalyst with neat fuel containing 0.5 g of Pb per gallon (simulating 16,000 miles). Study C aged the catalyst with 0.0625 g of Mn per gallon of neat fuel (simulating 24,000 miles). Study D, which simulated over 24,000 miles, aged the catalyst with repetitions of the following sequence: three simulated fill-ups of 0.0625 g of Mn per gallon, followed by one simulated fill-up of 0.80 g of Pb per gallon.

The catalyst used in this study was derived from a commercially available TWC for 1980 vehicles, with a Pt/Rh ratio of 11:1 and 40 g/ft<sup>3</sup> of precious metal loading. The catalyst used a Corning<sup>®</sup> substrate with 400 cells/in<sup>3</sup>. The catalyst buttons used in

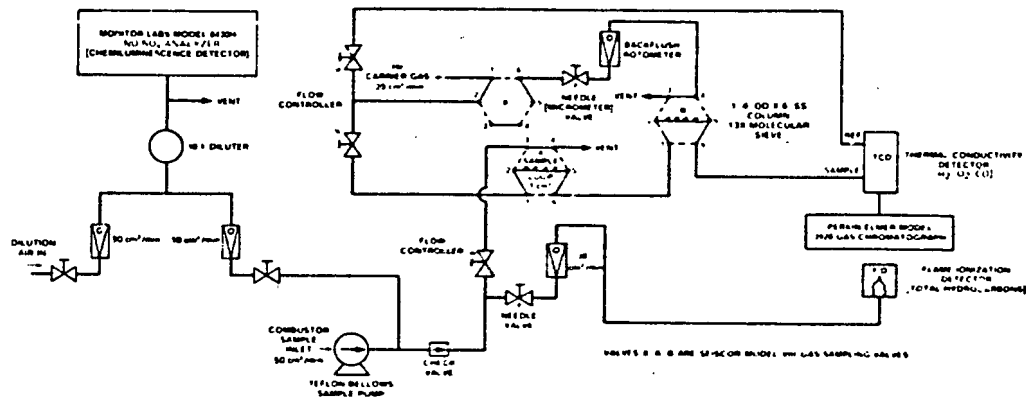


Fig. 3 - Gas analysis schematic

Table 1 - Comparison of Studies A, B, C, and D

Study	Aging		Evaluation <sup>a</sup>	
	Fuel	Conditions	Test Intervals (h)	Conditions
A	Neat: 70% Iso-octane 30% toluene 0.025% Sulfur	650°C catalyst temperature ~90,000 h <sup>-1</sup> space velocity	0, 30, 60, 90, 120, and 150	550°C catalyst temperature ~60,000 h <sup>-1</sup> space velocity
B	Neat + 0.5 g of Pb per gallon of fuel	650°C catalyst temperature ~90,000 h <sup>-1</sup> space velocity	0, 30, 60, 90, and 120	550°C catalyst temperature ~60,000 h <sup>-1</sup> space velocity
C	Neat + 0.0625 g of Mn per gallon of fuel	650°C catalyst temperature ~90,000 h <sup>-1</sup> space velocity	0, 30, 60, 90, 130, and 160	550°C catalyst temperature ~60,000 h <sup>-1</sup> space velocity
Db	Neat + 0.0625 g of Mn per gallon of fuel (fill-ups one through three)  Neat + 0.80 g of Pb per gallon of fuel (every fourth fill-up)	750°C catalyst temperature ~90,000 h <sup>-1</sup> space velocity	0, 30, 60, 90, 120, 150, and 160	600°C catalyst temperature ~60,000 h <sup>-1</sup> space velocity

<sup>a</sup>Base fuel alone was used for evaluation testing.

<sup>b</sup>Misfueling study.



the combustor studies were all hand-cut from the commercial TWC. These buttons, which were approximately 1.0 cm by 0.8 cm (diameter), fit snugly inside the quartz tube in the catalyst furnace.

The experimental conditions used in this study were 24,900 miles of vehicle operation simulated in 160 h of combustor aging. The MMT and TEL concentrations, which were based on a vehicle industry average fuel economy of 20 mi/gal, were twice the national average antiknock concentrations for automobile fuel. The increased concentrations of the antiknock additives that flow through the catalyst in the 24,000-mile simulation were assumed to be directly related to that of the national average concentrations in a 48,000-mile simulation. For example, during part of 1979, EPA suspended enforcement of its ban against use of the gasoline additive MMT, thus allowing refiners to use up to 1/32 g of MMT per gallon of fuel (0.031 g/gal) (14). In this study, 1/16 g of MMT per gallon of fuel (0.0625 g/gal) was used in two of the catalyst deactivation studies over 24,000 simulated miles.

#### RESULTS

In Study A, the catalyst button was aged for 150 h and evaluated with neat fuel containing 70% iso-octane, 30% toluene, and 0.25% sulfur. The catalyst was aged at 650°C and a space velocity of about 90,000 h<sup>-1</sup>, and was evaluated at 550°C and a space velocity of approximately 60,000 h<sup>-1</sup> at 30-h intervals. (The lower evaluation temperature was chosen to minimize the stress on the catalyst and to reduce the amount of aging while evaluating.) As shown in Figure 4, the catalyst activity or efficiency was slightly reduced throughout the simulation. Although the efficiency increased slightly between the 60-h and the 90-h evaluation, the slight downward trend continued beyond the 90-h evaluation. Table 1 describes the fuel content and test interval parameters for Studies A, B, C, and D. The catalyst button in Study B was aged for 120 h with 0.5 g of Pb per gallon added to the neat fuel. TEL caused a decrease in conversion efficiencies of HC and NO, as depicted in Figure 5. By the end of the 120-h simulation, HC efficiency was reduced from 90% to 64%, and NO efficiency was reduced from 95% to 48%.

In Study C, the catalyst button was aged for 160 h with 0.0625 g of Mn per gallon added to the neat fuel. Figure 6 shows that MMT primarily affected NO conversion efficiency; NO was reduced quickly after 60 h of aging to 26% efficiency by the end of the simulation.

Study D was planned to determine the effect of casual misfueling on the catalyst's NO reduction efficiency (15,16). This study aged the catalyst button with repetitions of three simulated fill-ups of fuel containing 0.0625 g of Mn per gallon of fuel followed by one simulated fill-up of 0.80 g of Pb per gallon of fuel. The aging fuel contents are

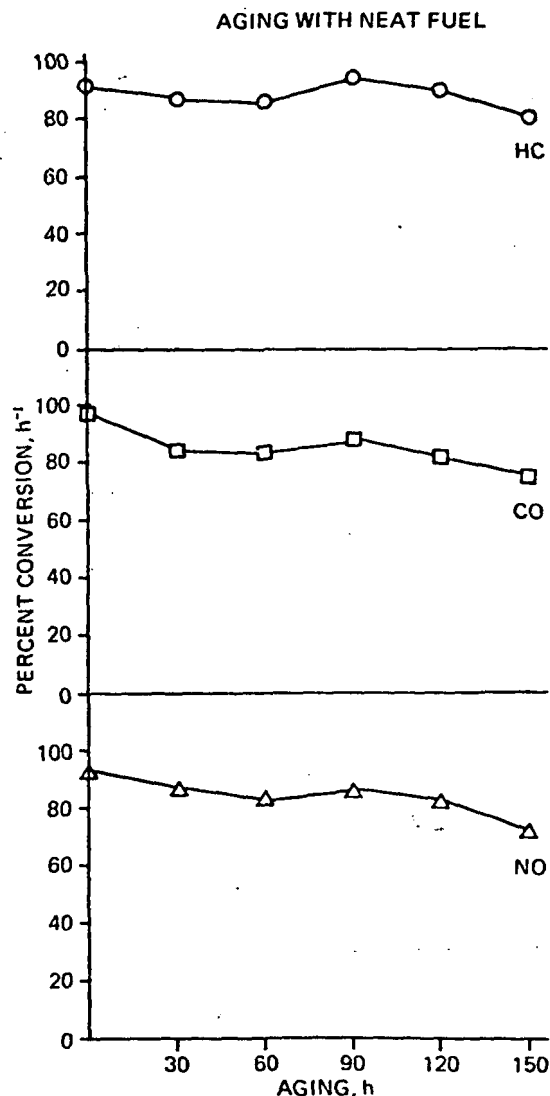


Fig. 4 - Study A: Three-way catalyst aged with neat fuel

shown in Table 1. The catalyst was aged at 750°C and a space velocity of about 90,000 h<sup>-1</sup> for 150 h. At 150 h of aging, the catalyst was aged for an additional 10 h with neat fuel to investigate the possibility of reactivation of the TWC in a poison-free atmosphere (i.e., no Mn or Pb present). The catalyst was evaluated at 30-h intervals at 600°C and a space velocity of about 60,000 h<sup>-1</sup> (temperatures recommended by the Automotive Catalyst Section of Engelhard Industries). Figure 7 indicates that the HC and NO conversion efficiencies were reduced at 150 h of aging; HC was reduced to 40% efficiency and NO was reduced to 18% efficiency. The HC and NO efficiencies increased slightly after aging in the poison-free atmosphere, but catalytic activity continued to be below 60% efficiency.