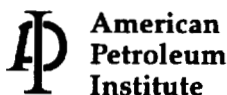


VEHICLE EMISSIONS TESTING OF RAPIDLY AGED CATALYSTS

Health and Environmental Sciences Department
Publication Number 4667
November 1997



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Vehicle Emissions Testing of Rapidly Aged Catalysts

Health and Environmental Sciences Department

API PUBLICATION NUMBER 4667

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EXECUTIVE SUMMARY

A test program was conducted to measure the effect of changing fuel sulfur content on the exhaust emissions of a 1993 Honda Civic VX certified to meet California Transitional Low Emission Vehicle (TLEV) standards. The type of exhaust aftertreatment device on this vehicle had been tested in prior programs sponsored by the Coordinating Research Council (CRC)(1)¹ and the Petroleum Environmental Research Forum (PERF)(2). The CRC study had generated debate as to how well the results represented "real world" conditions. The present test program provided an opportunity to address this question and related issues from the previous studies.

Exhaust emissions and catalyst oxygen storage (OSC) measurements were obtained on four catalysts designed for a 1993 Honda Civic VX TLEV. The measurements were made using two test fuels. One was a California emissions certification test fuel with a sulfur content of 35 ppm. This fuel was doped with additional sulfur to create a gasoline with a sulfur content of 600 ppm. The four catalysts included: (a) the original catalyst on the vehicle when purchased new; (b) two stock replacement catalysts which had been artificially aged to 100,000 miles on gasolines with 40 ppm sulfur and 1000 ppm sulfur, respectively; and (c) a "field-aged" catalyst obtained from an "in-use" 1993 Honda Civic VX TLEV with approximately 100,000 odometer miles.

The results of this test program show the following:

- The effects of sulfur on exhaust emissions of a 1993 Honda Civic certified to California TLEV standards were similar to those seen in other vehicle test programs such as those conducted by PERF and the Auto/Oil AQIRP. (1) (3) Emissions were lower on the 35 ppm sulfur fuel than on the gasoline with 600 ppm sulfur. The differences in emissions between fuels were statistically significant for the group of four test catalysts as a whole, but differences between fuels in individual catalysts were often not significant. Averaging over all catalysts, lowering fuel sulfur content from 600 to 35 ppm reduced FTP emissions by 21 to 27% depending on the pollutant.
- Exhaust emissions were lowest for the original catalyst and highest for the field-aged, 100,000 mile in-use catalyst (M9). The differences in emissions between the original catalyst and M9 were statistically significant for all pollutants over the FTP.

¹ Numbers in () denote references listed at the end of the report.

- Fuel sulfur content did not have an effect on the long-term emissions performance of catalysts which had been artificially aged using the RAT-A cycle. Catalysts M7 and M8 were aged for 100 hours on a dynamometer using the RAT-A cycle for 100 hours on 40 and 1000 ppm sulfur fuels, respectively. There was no difference in overall emissions or sulfur effects between these two catalysts.
- Rapid catalyst aging did not have a large effect on sulfur response compared to in-use aging. All catalysts responded directionally the same to sulfur and there was no difference in the magnitude of the sulfur effect among the four catalysts.
- An identical catalyst from a Honda TLEV was tested in the CRC Sulfur/OBD-II laboratory reactor program. A comparison of the data generated from the two programs suggests that laboratory results may (a) overstate sulfur effects as measured from a vehicle and (b) represent hot vehicle performance better than cold operation. Reducing fuel sulfur content from 600 to 40 ppm in the CRC laboratory reactor program lowered the Honda TLEV HC and NO_x emissions by 57% or more than twice the percentage effect seen over the FTP in the present study. However, the sulfur effects on HC that were observed during the warmed-up phases of the FTP (Bags 2 and 3) of the present study were similar to those measured in the CRC lab reactor program under steady-state, warmed-up conditions.
- Gasoline sulfur content did not have a significant effect on catalyst oxygen storage capacity. Differences in OSC between the original and the aged catalysts were much larger than any differences attributable to fuel sulfur content. OSC was roughly twice as high in the original catalyst compared to the three aged catalysts, all of which had similar OSC.

Section 1

INTRODUCTION

Over the past several years, interest in evaluating the effect of fuel sulfur content on motor vehicle emissions has prompted the initiation of a number of test programs which have focused on advanced technology vehicles.

In 1993, for example, the Petroleum Environmental Research Forum (PERF) sponsored a study to evaluate the effect of fuel sulfur content on exhaust emissions from low-mileage production vehicles designed to meet California's Transitional Low Emission Vehicle (TLEV) standards. (1) One of the TLEVs tested as part of that program was a 1993 Honda Civic VX.

An identical catalyst from a 1993 Honda Civic VX TLEV model also was tested as part of a recent study sponsored by the Coordinating Research Council (CRC). (2) The CRC project was designed to measure the effect of fuel sulfur level on the conversion efficiencies and oxygen storage capacities of various rapidly aged automobile emissions control catalysts. The measurements in that program were performed using a steady-state bench reactor because three of the four catalyst formulations that were tested were prototypes for which no suitable vehicle platforms were available at the time for FTP emissions tests. Equivalent fuel sulfur levels were obtained in the CRC program by varying the content of the SO₂ feedgas to the bench reactor. However, this raised the question as to whether the results of steady-state emissions tests performed in a laboratory bench reactor were truly representative of those which would occur under in-use transient conditions as measured by the Federal Test Procedure.

Since identical catalysts were used in the CRC and PERF studies, the 1993 Honda Civic VX TLEV model provided an opportunity for a further program to compare sulfur effects in "real world" conditions on a vehicle which had accumulated a history of emissions testing to those observed in a steady-state bench reactor. It also provided a means to determine if the catalyst aging procedures in the CRC program impacted the sulfur responses differently from vehicle aging of catalysts. This program was performed under contract to the American Petroleum Institute (API) by Chevron Research and Technology Co.

Section 2

TEST VEHICLES, CATALYSTS AND FUELS

TEST VEHICLES

Two vehicles were used in this test program and are described in Table 2-1. The first vehicle was a 1993 Honda Civic VX that was certified as a California Transitional Low Emissions Vehicle (TLEV). It is the same vehicle that was used in Petroleum Environmental Research Forum (PERF) Project 93-12. (1) At the time of the PERF testing, the odometer on this vehicle showed between 4,000 and 5,000 miles. In the current program, accumulated mileage on the 1993 Honda Civic VX was between 10,000 and 11,000 miles.

The 1993 Honda Civic VX was instrumented to permit exhaust samples to be drawn upstream of the catalyst and to measure temperature and oxygen content of exhaust before and after the catalyst. Since the vehicle was not equipped for California on-board diagnostics (OBD II), this included installation of a second exhaust gas oxygen sensor.

Table 2-1: Description of Test Vehicles

Model Year	1993	1996
Model	Honda Civic VX	Honda Civic LX
California Emissions Standard Certification	TLEV	LEV (OBD II)

The second vehicle was a 1996 Honda Civic LX loaned to the project by Honda R&D Americas, Inc. (HRA). This vehicle was an OBD II certified California Low Emissions Vehicle (LEV) and was used as a platform for obtaining catalyst oxygen storage measurements. The same catalysts tested on the 1993 model also were tested in this vehicle. HRA modified the exhaust manifold and catalyst plumbing on the 1996 test vehicle to enable use of a tool for diagnosing catalyst oxygen storage and release times.

TEST CATALYSTS

Four catalysts designed for use on a production 1993 Honda Civic VX model were tested in this program. (See Table 2-2.) The “original” catalyst was the stock catalyst originally installed on the 1993 vehicle and used in the prior PERF study. It was included in the current program primarily to provide a connection to the PERF study and to determine whether normal aging had influenced its tolerance for sulfur. Two new catalysts were provided by HRA. These were stock replacements for the original catalyst. They were aged by Southwest Research Institute using the RAT-A cycle for 100 hours. One catalyst was aged using California Phase 2 Certification gasoline. The other was aged using the same gasoline with sulfur level raised to 1000 ppm. (See Appendix A for a description of the aging procedure used by SwRI.) HRA also provided a catalyst which they had obtained from a customer. This catalyst had been taken from a 1993 Honda Civic VX which had accumulated 107,000 odometer miles in customer service.

Table 2-2: Test Catalysts

Catalyst Code	Catalyst Description
ORIG	OEM Catalyst used in PERF study
M7	Replacement catalyst aged 100 hrs on 40 ppm S on RAT-A cycle
M8	Replacement catalyst aged 100 hrs on 1000 ppm S on RAT-A cycle
M9	100k catalyst aged in field in customer use

TEST FUELS

Two test fuels were used in this program. The base fuel was a California Phase 2 Certification gasoline containing about 35 ppm sulfur. The second test fuel was made by spiking the base fuel with di-*tert*-butyl disulfide (DTBS) to achieve a level of about 600 ppm sulfur. Inspection results are listed in Table 2-3.

Table 2-3: Test Fuel Analyses

Fuel Property	Fuel Code	
	FR12652	FR24491
Sulfur, ppm	35	600
API Gravity	60.1	not measured
Aromatic, Vol. % (uncorrected FIA)	25.8	not measured
Olefin, Vol. % (uncorrected FIA)	5.4	not measured
Paraffin, Vol. % (uncorrected FIA)	68.8	not measured
Hydrogen, Mass Fraction (NMR)	.1365	not measured
D86 T ₁₀ , ° Fahrenheit	139	not measured
D86 T ₅₀ , ° Fahrenheit	205	not measured
D86 T ₉₀ , ° Fahrenheit	294	not measured
MTBE, Vol. %	10.8	not measured