Measurement of Atmospheric Reactivity of Emissions from Gasoline and Alternative Fuel Vehicles

Subcontractor

Coordinating Research Council

Principal Investigator

Nelson A. Kelly
Environmental Research Department
GM R&D Center, MC 480-106-269
30500 Mound Road
Warren, MI 48090-9055
(810) 986-1623

DOE Project Manager

Michael Gurevich
U.S. Department of Energy
CE-332, MS 6A-116/Forrestal
1000 Independence Avenue, SW
Washington, DC 20585
(202) 586-6104

NREL Technical Monitor

Brent Bailey
NREL
1617 Cole Boulevard
Golden, CO 80401-3393
(303) 275-4468

Subcontract Number

AF-2-11296-01

Performance Period

6/92–4/96

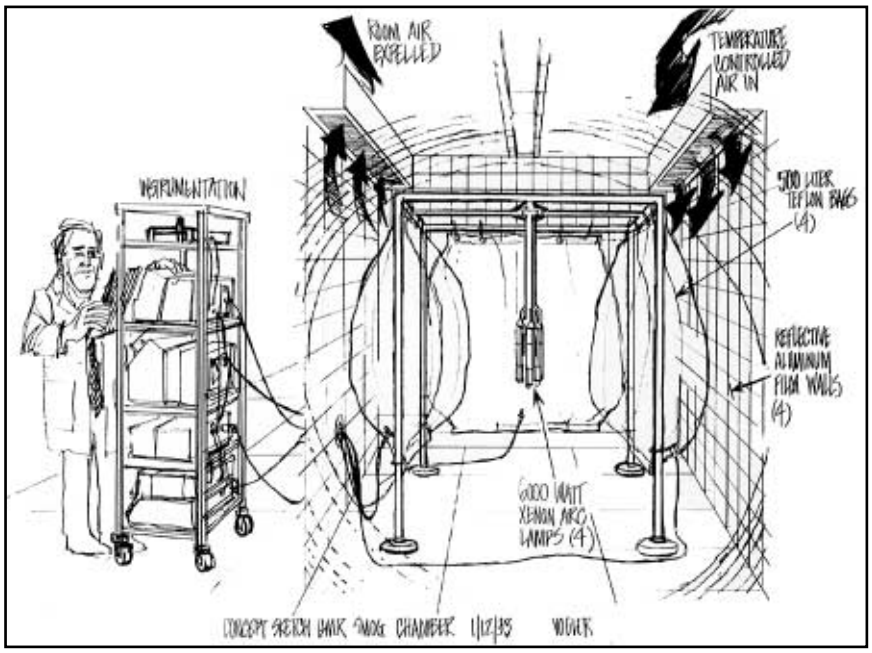
NREL Subcontract Administrator

Scott Montgomery (303) 275-3193

Objective

The capacity of various volatile organic compounds (VOC's) to form different amounts of ozone (O_3) in the atmosphere is referred to as reactivity.

Recent California vehicle-exhaust emission regulations include the use of reactivity to determine compliance with the VOC portion of the regulations. California has chosen the Carter maximum incremental reactivity (MIR) factors to calculate the exhaust reactivity. Carter factors have been computed for individual exhaust VOCs using a model of the ozone formation process.



GM smog chamber facility

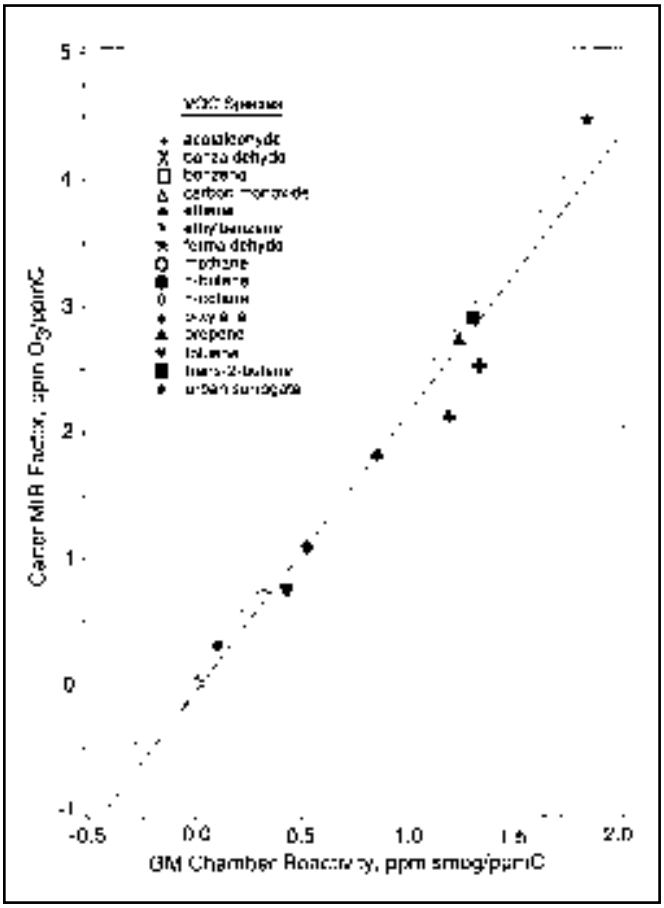
The main objective of our study was to measure the reactivity of a series of compounds representative of those found in vehicle exhaust, and to compare the measurements to the Carter MIR factors. To measure reactivity we used a set of smog chambers with conditions approximating those used in the Carter MIR factor derivations.

Approach

A sketch of the GM chamber facility is shown in the first figure. In a typical reactivity experiment, four identical chambers were filled with a standard urban mixture containing nine VOCs to represent polluted urban air (this was called the "urban-surrogate" mixture) plus NO_x; the initial VOC/NO_x ratio of the standard urban mixture was five. Small amounts of a test compound were added to three of the four chambers. The amount of NO oxidized and ozone formed, which is referred to as the smog formation, was monitored in each chamber during a 12-hour irradiation. By comparing smog formation in the three test chambers to that in the remaining chamber, which contained only the standard urban mixture, the incremental reactivity of the test compound was measured.

Accomplishments

The results of a series of experiments to measure the reactivities of 14 individual compounds, as well as the nine-component "urban-surrogate" mixture, are compared to the Carter MIR factors in the second figure. The 14 test compounds, which are representative of those found in the exhaust from gasoline-fueled vehicles, covered a wide range of reactivities and atmospheric oxidation mechanisms. For example, methane has a low reactivity and a simple oxidation mechanism, formaldehyde has a very high reactivity due to its photodissociation to produce radicals, and benzaldehyde has a negative reactivity since it removes radicals and NOx from the system. In the list of compounds studied, the aromatic compounds have the least well understood atmospheric chemical mechanisms.



Carter MIR factors versus reactivities measured in the GM smog chambers for 14 individual test species and the urban-surrogate mixture

The major finding in this study was that the experimentally-measured reactivities showed a high correlation with the Carter MIR factors, as shown in the second figure. Thus, it appears that the photochemical model used to derive the Carter factors correctly predicts the relative reactivity, even for compounds with uncertain mechanisms, such as toluene, p-xylene, and ethylbenzene.

Future Direction

Over 150 experiments were conducted during the course of the two-year study. The experiments included reactivity measurements of simple mixtures, of exhaust mixtures, and of individual compounds as a function of temperature. In addition, over 50 experiments were run to characterize the smog chamber wall conditions and light intensity. This complete data base will be used to test the detailed chemistry in photochemical models.

Publications

Kelly N. A. and P. Wang . "Indoor Smog Chamber Measurements of Incremental Reactivity Factors," presented at the Fourth U.S./German/European Workshop on the Photochemical Ozone Problem and its Control, Charleston, South Carolina, June 13, 1994.

Kelly N. A. and P. Wang . "An Experimental Evaluation of the Integrated Empirical Rate Model," presented at the Fourth U.S./German/European Workshop on the Photochemical Ozone Problem and its Control, Charleston, South Carolina, June 16, 1994.

Kelly N. A. and, P. Wang . "Measurement of the Atmospheric Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies. Part 1—Indoor Smog Chamber Study of Reactivity," First-year final report dated June 30, 1994. Available from the Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta GA.

Kelly N. A. and P. Wang . "Smog Chamber Measurements of Exhaust Reactivity," presented at the Fifth CRC On-Road Emissions Workshop, San Diego, CA, April 5, 1995.

Kelly N. A. and P.Wang . "Smog Chamber Measurements of Incremental Reactivity," presented at the Workshop on Chemical Mechanisms Describing Oxidation Processes in the Troposphere, Valencia, Spain, April 27, 1995.

Kelly N. A. and P. Wang . "Measurement of the Atmospheric Reactivity of Emissions from Gasoline and Alternative-Fueled Vehicles: Assessment of Available Methodologies. Part 1—Indoor Smog Chamber Study of Reactivity," Second-year final report dated June 13, 1996. Available from the Coordinating Research Council, Inc., 219 Perimeter Center Parkway, Atlanta, GA.

Kelly N. A. and P. Wang . "Comparison Between Smog Chamber Measurements and Theoretical Predictions of Reactivity," Paper No. 96-WP62B.01, presented at the 89th Air and Waste Management Association Meeting, Nashville, TN, June 26, 1996.