



Project Summary

Exhaust Emissions from a Diesel Engine

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Studies were performed using (1) diesel particles collected from the undiluted exhaust of a single-cylinder engine, operated at constant speed and load, using a binary pure hydrocarbon fuel with air or gas mixture oxidizers, and (2) diesel particles collected from the diluted exhaust of a multicylinder engine operated on a commercial fuel. The physicochemical properties of the particles were determined by static and dynamic methods. The organic adsorbate was characterized by gas chromatography and mass spectrometry and by microbial testing protocols. Electron paramagnetic resonance spectrometry and high performance liquid chromatography were used to study reactivity of the organic adsorbate.

The particles collected from the exhaust of diesel engines operated on a 1:1 mixture of 2,2,4-trimethylpentane and n-tetradecane and on commercial fuels contained similar compounds in their organic adsorbates. The nitrogen in these compounds is derived mainly from the oxidizer (air).

Diesel particles have high surface areas and reactivities; this results in the efficient collection of organic adsorbates. The heats of adsorption of the organic adsorbates on the surface of diesel particles are sufficiently large that these molecules are not released into the biological solvents used in microbial testing protocols testing for cytotoxic effects.

The microbial mutagenic activities of the organic adsorbates found on the surface of both types of diesel particles are comparable. These microbial mutagenic activities can be attributed mainly to the presence of nitrated polynuclear aromatic hydrocarbons.

This Project Summary was developed by EPA's Environmental Sciences 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

A number of studies have been performed on the organic extracts of collected diesel engine particulate matter. These studies indicated that the organics associated with this particulate matter have biologic activity. However, the source of this activity was not identified. Attempts to define the origin and nature of the compounds responsible for these effects and the ultimate implication of this activity were confounded by the complexity of the diesel fuel. Although a variety of extraction systems were used to study the carbon particulate, its basic character was unknown.

This study was undertaken to define the surface character of the carbon particulate matter emitted from diesel engines and to identify combustion products by using pure fuel and oxidizer components to simplify the emissions. The use of controlled pure components aids product identification by limiting the number of possibilities and interferences from fuel compounds. A wide variety of analytical techniques, such as gas chromatography, gas chromatography/chemical ionization mass spectrometry, and high performance liquid chromatography, were used to chemically identify the products. The Ames test and the Comptest were used to measure biologic activity.

The study was divided into four main components. Three of the components

were engineering, design, and operation of the engine using various fuels and oxidants; chemical analysis of the adsorbed organics on the particulate matter; and biologic assay of the particulate and associated organics. The fourth component, physical chemical characterization of the particulate matter, was treated separately, although particulate matter generated by the other components was one of the three types of particulate studied. Very few studies have attempted to accurately define the physical chemistry of particles in diesel exhaust.

As a result of this study, nine papers were published in peer-reviewed journals. The final project report incorporates information in those papers and may provide more detail on some aspects of the study.

Procedure

An AVCO-Lycoming Bernard W-51 industrial diesel engine was used for the study. The small, single cylinder, four-stroke, air-cooled direct-injected diesel engine was operated at 2,400 r/min on a 1:1 mixture of 2,2,4-trimethylpentane and n-tetradecane. This pure fuel had a measured cetane number of 53.4. A synthetic lubricant, polyalkyleneglycol (UCON LB 525, Union Carbide), was used for the engine and was maintained at 60°C.

The engine emissions were mixed and a continuous aliquot of approximately 17% was taken. This aliquot was cooled through a heat exchanger to below 52°C and filtered to remove the particulate carbon monoxide, carbon dioxide, oxygen, NO/NO_x, and hydrocarbons were measured. A constant flow was maintained by a series of pumps and meters, and the particles were collected on Teflon coated, glass fiber filters.

A series of different air oxidizing systems containing 5 or 10% excess oxygen and 10% excess nitrogen were used. A special nitrogen free blend of 18.9% oxygen, 20.7% argon, and 50.4% carbon dioxide was chosen to simulate the physical characteristics of air. In all cases, the amount of oxygen relative to the amount of fuel (oxygen/fuel ratio) was held constant and the volume of gas used was adjusted to conform to the percentage composition, i.e., supercharging.

Filter samples were collected until 0.1 to 0.2 gram of particulate was obtained (10 to 20 minutes). Filters were dessicated to equilibrium, weighed, and stored in a refrigerator. They were protected from light.

Organic extracts of the particulate were prepared by methylene chloride extraction for 24 hours at two cycles per hour. The extract was reduced to dryness using a rotating evaporator and purging with dry nitrogen or argon. The extract was stored in vials and refrigerated. It was protected from light.

Extracts were analyzed by gas chromatography (GC), gas chromatography/chemical ionization mass spectrometry (GC/MS), and high performance liquid chromatography (HPLC) with MS identification. The gas chromatograph used a 0.25 mm i.d. borosilicate glass column (WCOT) coated with SE-54 with either a flame ionization or a nitrogen specific thermionic detector. Nitrogen or helium was used as the carrier gas, as appropriate. The column was temperature programmed for 100° to 300°C at 2°C/minute.

The gas chromatograph for the GC/MS system was similarly configured. The chemical ionization mass spectrometer (CIMS) was operated in both the positive and negative ionization mode with automatic computer controlled data collection. Some comparison runs were made on a different system using electron impact ionization and similar GC systems. The spectra obtained from these systems were compared with those at the National Bureau of Standards MS Library.

HPLC was used for fraction separation before analysis using a 5- μ m silica column with a multisolvent program: n-hexane programmed to 100% dichloromethane in 10 minutes and then programmed to 100% acetonitrile in 10 minutes. A 254-nm ultraviolet (UV) detector was used. Fractions were collected, evaporated to dryness, and analyzed on the CIMS using a programmable direct insertion probe.

Environmental Protection Agency (EPA) personnel analyzed for nitropyrene using HPLC with on column reduction to aminopyrene and fluorescence detection. Biological testing was conducted on the soluble organic extracts of the particulate matter and on the total particulate. Two microbiological assays were used in this study: the Ames test and the Comptest. The Ames test was conducted with tester strains TA98 and TA100 with and without S9 metabolic activation, according to the standard procedures developed by Dr. Ames. The Comptest was conducted on *Bacillus subtilis* RUB827 and RUB818 wild type (as reported by R. E. Yasbin in *Environ. Mutagen.*, 1981).

The diesel particulate collected during tests was examined with respect to its

physical chemistry and compared to diesel particulate collected from a diesel engine operating on conventional cycles using full-boiling-range (regular) number two diesel fuel and commercial lubricating oil. A graphitized carbon black fuel (Spheron 6) was chosen as a reference.

Particle size was measured by electron microscopy (EM) and the external surface area was calculated. Bulk and helium densities were determined when sufficient sample was available. Brunauer, Emmett, and Teller (BET) surface areas were calculated with nitrogen (16.2 A²/molecule), benzene (40 A²/molecule), and n-hexane (51 A²/molecule). A number of preconditioning regimes were followed to vary the activation temperature and other conditions. GC was used to determine the isothermic heats of adsorption for a wide variety of compounds. Additional efforts were made to define the surface character of the particulate matter using electron paramagnetic resonance spectrometry with and without UV radiation.

Results

Engine Operation, Chemical Analysis, and Biologic Assay

Use of the nitrogen free oxidizer results in reduced power and delayed ignition. No oxides of nitrogen were present in the exhaust, and total hydrocarbons and particulates were reduced 40 to 30%. When nitrogen was present, carbon monoxide and total hydrocarbons decreased as the percentage of oxygen increased. The nitric oxides increased to a maximum at 25% oxygen and then decreased slightly. The total amount of particulate decreased with increasing oxygen while the percentage of soluble organics increased.

Forty-five organic compounds were detected on the particulate matter by GC; 10 of these compounds could not be positively identified, although an estimation of molecular weight was possible from the CIMS. Twenty polynuclear aromatic compounds, ranging from naphthalene to benzo(ghi)perylene, were detected as well as 11 compounds containing oxygen: two furans, two quinones, and seven carbonyl compounds. The fuel component n-tetradecane, phthalate anhydride, benzo(c)cinoline, and nitropyrene were also seen.

The oxidizing system variation influenced the chemical composition of the particulate. When the nitrogen free oxidizer was used, the oxides of nitrogen decreased from an average of 470 ppm to

less than 1 ppm. Most of the nitrogen containing compounds were eliminated, and those remaining were at concentrations that were too low to identify. The components identified from the runs using the air oxidizer were very similar to those seen from regular diesel fuel even though only a two-component mixture was used.

The presence of 1-nitropyrene was not correlated with the presence of either nitric oxide or nitrogen dioxide, and it was not related to the presence of pyrene in the sample. Furthermore, no overall relationship existed between 1-nitropyrene and the amount of total particulate. This finding is different from previous observations of particulate matter that was collected from experiments using the nitrogen free oxidizer and exposed to a stream of nitrogen dioxide and water vapor. In these experiments, the amount of 1-nitropyrene increased as the concentration of nitrogen dioxide increased.

The results from the chemical analysis are consistent with the biologic activity results, which correlate well with the amount of nitropyrene present in the nitrogen containing systems. Very few nitropyrenes were present in the nitrogen free case and almost no biologic activity was detected. When nitrogen dioxide was added to these particles, a large step increase in activity occurred, and increasing nitrogen dioxide caused a gradual increase in activity. No significant increase occurred in any of the tests that involved biologic activation (+S9) and in many cases, the results were lower. This result indicates that the activity was direct acting. The amount of nitropyrene in the system could not account for the activity observed; therefore, other compounds must cause the additional activity.

A 10- to 20-fold increase in activity occurred between the nitrogen free and air oxidant cases. Toxicity also increased but was not severe enough to interfere with any tests. Very similar results were seen from the Comptest. The fuels and lubricants used showed no activity in any system.

Attempts were made to test the unextracted particles; however, no positive results were obtained. These results were compared to test results from unextracted particles collected from an identical engine operated on regular diesel fuel and lubricant with air oxidant. These tests were slightly positive in strains TA98 and TA100 at similar levels to those seen for the organic extracts of the particles obtained from the nitrogen free oxidizer.

Physical Chemical Characterization

The results from the EM and BET (nitrogen) tests are summarized in Table 1. The roughness factor is the ratio of the two area determinations and may be taken as an indication of porosity. In this case, the diesel particles from regular fuel are much less porous than the carbon black (Spheron 6) particles.

The engine particulates from the regular diesel fuel and from the pure fuel exhibited distinct differences. The surface area and the type of adsorption for both types of particulate were strongly dependent upon temperature of activation and only reached the value shown in Table 1 after activation and degassing at 400°C. At lower temperatures, the surface of the regular fuel particulate appeared to be already covered and not subject to classical adsorption. This idea was further supported by a net weight loss of 17.5%, which is approximately the amount of material that can be extracted by using

dichloromethane. In contrast, the particulate matter from the pure fuel studies showed the largest surface area initially and this area was reduced on each successive run with benzene or hexane. Higher activation temperatures up to 400°C temporarily increased the area but not to the original levels, possibly indicating some very strongly adsorbed material that could not be removed under the described conditions.

Heats of adsorption showed a similar phenomenon. This response indicated that the surface of the particulate from the diesel engine using regular fuel was already covered and that after 400°C activation, a fresh surface was exposed and normal monolayer coverage occurred. This normal situation prevailed for the carbon black and pure fueled diesel engine particulates.

A dynamic GC method to measure isothermic heats was employed by using the particles as the column. The method allowed use of a wide variety of conditions and materials. Test results are shown in Table 2.

Table 1. EM and BET Test Data

Particulate Source	Density g/cm ³	Diameter nm	Surface Area Calculated From (EM) m ² /g	BET Surface m ² /g	Roughness Factor
Pure fuel	-	36	86.7	103.7	1.2
Regular fuel	1.5 -1.8	26.8	116.1	112.2	0.97
Carbon black (Spheron 6)	1.85-2	410	76.9	110	1.43

Table 2. Isothermic Heats of Adsorption

Adsorbate	Heat of Vaporization (kcal/mole)	Heat of Adsorption (kcal/mole)		
		Diesel Particulate Matter This Study	DPM-EPA	Graphitized Carbon Black*
Water	9.72	10.3	6.9	5.6
Methanol	8.98	9.0	4.8	5.3
Dichloromethane	-	8.6	5.0	-
n-Hexane	7.63	11.4	15.0	10.4
1-Hexane	7.79	10.6	10.2	-
Benzene	8.15	12.0	12.8	9.8
Cyclohexene	-	10.2	9.7	9.1
Cyclohexane	7.83	8.7	9.3	8.7
Ethylbenzene	9.3	15.2	8.3	12.7
Acetophenone	11.73	16.1	15.1	13.0
Benzaldehyde	11.66	17.4	12.2	-
n-Octane	9.2	15.2	8.4	13.4
Phenol	11.89	16.4	12.2	13.0
Naphthalene	12.31	16.4	12.3	17.3
Anthracene	16.82	-	11.1	-
Phenanthrene	14.18	-	19.0	-

*These data were obtained from Gas Adsorption Chromatography (Kiselev, A. V., and Yasbin, Y. I. New York: Plenum Press, 1969).

Electron paramagnetic studies were made on all particles to determine surface character and interactions. In general, the spin concentrations were similar for the two diesel particle samples and for carbon black, as reported in the literature. The addition of oxygen or nitric oxide caused an expected decrease in the signal. Nitrogen dioxide caused no immediate effect but showed a strong increase with 24-hour exposure, indicating that reactions leading to paramagnetic species has occurred. Irradiation by UV light affected the surface activity; the degree of effect depended upon conditions and pressure in the system as well as the nature of the components. The most significant change was a 30 to 50% increase observed when the sample was maintained in a vacuum.

Conclusions and Recommendations

Diesel engines operated with pure component fuels have similar emissions to vehicles operated with full-boiling-range diesel fuels. The soluble organic matter associated with the particulates from pure component fuels, although simpler in composition because of the absence of the multiplicity of fuel components, has many of the polynuclear aromatic compounds and other organic species that result from full-boiling-range fuels. The particulates resulting from pure fuel and from regular fuel also have similar biologic activity.

Operation of the diesel engine on a nitrogen free oxidizer demonstrated that the biologic activity was reduced by over an order of magnitude. This biologic

activity was correlated to nitropyrene, although the concentration of nitropyrene was insufficient to account for activity. The amount of nitropyrenes present did not correlate with the amount of nitrogen dioxide present. When particles obtained from the nitrogen free experiments were exposed to nitrogen dioxide, the amount of nitropyrene and the biologic activity increased with increased doses of nitrogen dioxide.

The surface character of the particulate matter generated by the pure component fuels was similar to that of regular diesel fuel particulate. Both were comparable to carbon black fuel in surface area but with somewhat higher activity for many compounds. The particles were shown to have a multilayer coating of organics and they were characterized by dissolution in the organic coating rather than monolayer adsorption.

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The complete report, entitled "Exhaust Emissions from a Diesel Engine," (Order No. PB 84-122 910; Cost: \$13.00, subject to change) will be available only from:

National Technical Information Service

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