Emissions Characteristics of Soy Methyl Ester Fuels in an Underground Mining Diesel Engine with and without Diesel Oxidation Catalyst Aftertreatment

Final Report for the National Biodiesel Board

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EXECUTIVE SUMMARY

This report summarizes the testing of soy methyl ester (SME) fuels by the U.S. Bureau of Mines (USBM) during 1994. The work was conducted under agreements with the National Biodiesel Board, the Agriculture Utilization Research Institute, and the U.S. Department of Agriculture.

Testing Program

The emissions and combustion characteristics of methyl ester fuels were evaluated in an indirect injection diesel engine that is typical of engines used in underground mines. Three fuels were tested: 100% (neat) SME fuel, a commercially available, low sulfur, #2 diesel fuel (D2), and a blend of 30% SME and 70% D2 fuels. All fuels were tested with transient tests, where an engine's speed and load are constantly varied in a repeatable cycle, and with the International Organization for Standardization (ISO) 8178-C1 steady-state test, where an engine's speed and load are held constant and the engine is tested at several conditions.

Methyl ester fuels have been shown to decrease the nonvolatile, carbonaceous soot fraction (NVOL) of diesel particulate matter (DPM), but they increase the adsorbed or condensed volatile organic fraction (VORG) of DPM. For this reason, diesel oxidation catalysts (DOC) were included in this test program. DOCs can reduce the VORG and provide significant decreases in total DPM. An older formulation Engelhard DOC and an advanced formulation Engelhard DOC were tested. The advanced formulation DOC was commercialized recently, in part because of this testing program, as an oxygenated fuels catalyst under the trade name Bio-Cat.

Evaluations included total DPM by gravimetric analysis, VORG and NVOL fractions of DPM, major exhaust gas constituents, particle size distributions, fuel consumption and power, and basic combustion phenomena to help explain emissions results.

Results

Methyl ester fuels decreased NVOL but increased VORG, causing an overall DPM decrease of approximately 30% when neat SME was compared to D2. No significant difference was noted for the blend fuel. Neat SME and the blend tended to decrease emissions of hydrocarbons and sometimes carbon monoxide (CO). Small decreases in NOx emissions were noted for both fuels for some conditions, but no significant NOx increases occurred with any methyl ester fuel. Small decreases in formaldehyde occurred with the use of the methyl ester fuels for some conditions. NO2 was mostly unchanged except for decreases with the use of neat SME fuel during the transient tests.

The DOCs had similar emission reduction efficiencies for hydrocarbons and CO, but differed with respect to other emissions. Both DOCs provided 60 to 90% reduction in CO and hydrocarbons, depending on the conditions. The older formulation DOC produced more sulfates than the advanced DOC, and in some cases this caused the total DPM to increase for D2 and the blend. The older DOC was also not as efficient in reducing VORG. The advanced formulation DOC, when combined with neat SME, provided a decrease in total DPM of 60 to 65%. The advanced DOC combined with the blend fuel provided a decrease in total DPM of 30 to 40%. Both DOCs increased NO2 when used with neat SME, but the older formulation DOC produced much more
N\textsubscript{2} and also caused NO\textsubscript{2} to increase by an order of magnitude when D2 was used. Also, the advanced DOC decreased NO\textsubscript{2} emissions during the cool (light-duty) transient for all fuels.

Chemical and biological analyses indicate that most of the methyl ester fuel is comprised of hydrocarbon chains chromatographically equivalent to C19 and C21 alkanes. Hydrocarbons at C14 to C18 and above typically condense onto the DPM, while shorter chain hydrocarbons remain in the vapor phase. If unburned fuel is remaining intact in the exhaust stream, it may help explain the VORG increases with methyl ester fuels.

Combustion analyses indicate that the pre-mixed burn fraction of combustion is decreased with the use of methyl ester fuels. Most of the NO\textsubscript{x} formation takes place in the pre-mixed burn fraction, so a decrease may explain the NO\textsubscript{x} decreases that were observed. Also, the peak temperature of combustion decreased with the use of the methyl ester fuels because of their lower energy content, which may also explain the decreases in NO\textsubscript{x}. Because of the lower energy content of the fuel, neat SME had 9% less power and had an increase in fuel consumption of 13%. The blend fuel showed a 4% decrease in power and a 4% increase in fuel consumption.

Results from this project will be used for publication and presentation at the Society of Automotive Engineers International Congress and Exposition in February 1995, SAE paper 950400 (paper in press).
Diesel-powered equipment is used in underground mines because it is more powerful and mobile than electric-powered equipment. However, diesel emissions in the enclosed environments of underground mines pose a significant health hazard to mine workers. The health risks associated with exhaust gases have been well documented. The National Institute for Occupational Safety and Health and the International Agency for Research on Cancer (IARC) respectively have declared whole diesel exhaust to be "potentially" or "probably" carcinogenic. Currently, the Mine Safety and Health Administration (MSHA), the regulatory agency overseeing U.S. mines, has set exposure limits for the primary diesel exhaust gases and is proposing lower permissible exposure limits including lower standards for NO, NO₂, and formaldehyde (HCOH).

Diesel particulate matter is also a significant health hazard in underground mines. MSHA has proposed new standards for the use of diesel equipment underground and is expected to set an exposure limit for DPM of 0.5 mg/m³ or even as low as 0.2 mg/m³. Compliance with a low permissible exposure limit for DPM will pose a significant challenge for diesel equipped mines.

The U.S. Bureau of Mines has developed and/or evaluated technologies for reducing exhaust exposures in underground mines. These technologies include exhaust aftertreatment devices, engine maintenance, fuels and fuel additives. Exhaust aftertreatment devices include particulate traps, catalytic converters, and disposable DPM filters. - Some aftertreatment devices have limitations with respect to certain mining applications. They can also be relatively expensive. The disposable filters often used on coal mine face equipment cost between $2 and $4 per hour of equipment operation or approximately $0.07 to $0.09 per ton of coal mined.

This paper describes the results from a laboratory evaluation of soy methyl esters that have the potential to reduce emissions in underground mines. The primary objective of the evaluation was to compare and characterize gaseous and particulate emissions from a heavy-duty diesel engine using a low-sulfur D2 fuel, a methyl ester blend, and a 100 % methyl ester fuel. Performance was evaluated with and without diesel oxidation catalysts to optimize emission reductions. Secondary objectives were to characterize basic combustion phenomena (heat release) and DPM size distributions to help explain emissions and performance results.

About 40 to 70% of the total DPM mass is made up of agglomerations of carbon spherules. Hydrocarbons adsorbed or condensed onto the carbon agglomerates account for 30 to 60% of the DPM mass. The condensed and adsorbed hydrocarbons are usually referred to as the soluble organic fraction (SOF), or the volatile organic constituents (VORG). Because the contribution of hydrocarbon constituents to the total mass of DPM is highly temperature dependent, DPM is defined as the filterable material at a temperature below 52 degrees C. The typical filter temperature during the transient portion of this test program was approximately 45 degrees C, and the typical filter temperature during the steady-state testing was 35 degrees C, but varied depending on the mode. Depending on the fuel and aftertreatment, up to 20% of the DPM mass can be made up of volatile and nonvolatile sulfates.

The inhalation of DPM in mines is a significant health concern of the USBM. Control and monitoring of DPM in underground mines is a major focus of research within the Health Research Division of the USBM. Many of the compounds present in the adsorbed and condensed
hydrocarbon portion of DPM are known or suspected carcinogens. Examples of these include polynuclear aromatic hydrocarbons (PAH). More than 90% of diesel particulate has an aerodynamic diameter of less than 1 um. Particles with aerodynamic diameters less than 2 um are 90 to 100% respirable. Evidence from epidemiological studies and animal experimentation show a correlation between the inhalation of fine aerosol particles, including DPM, and the incidence of lung cancer. It is unclear as to whether particle size, the mass of elemental carbon, or chemical composition of the adsorbed and condensed compounds plays a predominant role in possible damage to the lungs. However, toxicological studies have shown that rats exposed carbon black spheruies (containing little or no adsorbed hydrocarbon material) develop lung tumors at the same rate as rats exposed to whole diesel exhaust, possibly indicating that carcinogenicity is related more to the carbon fraction of DPM than the organic fraction.

Methyl Ester Diesel Fuels

Previous investigations have shown that oxygenated fuels such as SME may reduce DPM emissions. However, tests have also shown that using chemically unaltered vegetable oils as a diesel fuel or a diesel fuel extender cause engine problems or require engine modifications. Neat vegetable oils (soy, sunflower, canola) are composed primarily of glycerol esters of fatty acids (triglycerides). Kinematic viscosities of these oils are typically about 25 to 35 centistokes (cSt) versus the American Society for Testing and Materials (ASTM standard D975 values of 1.9 to 4.1 cSt for number 2 diesel fuel. These differences reduce fuel atomization, increase fuel penetration into the combustion chamber (prior to vaporization) and cause combustion abnormalities unless significant changes are made to the fuel delivery system and the design of the combustion chamber. The use of triglyceride-based vegetable oil fuels can lead to contamination of the crankcase oil with unburned fuel. Fuel impingement on the piston crown and cylinder walls when using triglyceride fuels can cause the formation of deposits made up of carbon and polymerized organic compounds. With extended use, this can lead to piston and piston ring deposits, ring sticking, and eventually, engine failure.

When neat vegetable oils are emulsified with ethanol, butanol or other alcohols and diesel fuel or mixed in concentration of less than 50% with diesel fuel, the viscosity of the resulting fuel mixtures is only marginally higher than the typical viscosity range for petroleum diesel fuels. However, tests with vegetable oil-diesel fuel mixtures and vegetable oil-methanol-diesel fuel emulsions have revealed problems. Concentrations of 25% neat vegetable oil within an emulsion have caused engine durability problems due to fuel injection nozzle coking, polymerization of fuel components, and piston and ring deposits.

Over the last 10 to 15 years, methyl and ethyl esters of various vegetable and seed oils and animal tallow have been proposed as possible diesel fuels or fuel extenders. These are produced by transesterification, a chemical process in which one alcohol component of an ester is chemically replaced by another. In the case of vegetable oils, the glycerol components of the triglyceride molecules are exchanged for lighter alcohols such as methanol ethanol (figure 1). The result of the process is a product composed of fatty acid methyl esters, which consist of straight saturated and unsaturated hydrocarbon chains with a carbon number of 18 or 19, containing an additional carboxyl group (figure 2). The methyl esters have a kinematic viscosity that is similar to, or slightly higher than, the ASTM D975 standard for number 2 diesel fuel. Methyl esters are completely miscible in diesel fuel and thus can be blended with current petroleum-based fuels. The transesterification process typically result in methyl esters of about 90 to 97% purity after water washing. The remaining 3 to 10% contains a combinat
of mono-, di-, and triglycerides, free fatty acids, and glycerine. These remaining impurities can be removed by distillation.

The primary technical interest with methyl ester fuels is their ability to reduce DPM emissions. This occurs through reduction of the insoluble or nonvolatile carbon soot portion of DPM. Similar results have been obtained through the use of other diesel fuel oxygenates and by oxygen enrichment of intake air. The soot reduction could be caused by increased oxygen availability to locally fuel-rich regions of the combustion chamber. Tests of petroleum diesel fuels with oxygenate additives have shown an almost linear decrease in DPM emissions as fuel oxygen content was increased over a range from 0 to 2.5% (by mass) primarily by reducing carbon soot constituents. The testing also showed an increase in emissions of oxides of nitrogen (NO) as the fuel oxygen content was increased. Tests with methyl ester fuels have typically shown a reduction in smoke opacity, as would be expected to accompany reductions in carbon soot emissions. Decreases, increases, and similar total DPM emissions levels have been reported for various methyl esters and blends of methyl ester with petroleum diesel fuels. The VORG has tended to increase as more methyl esters are present in fuel blend. Sometimes this increase in VORG is larger than the decrease in carbon soot and a net increase in DPM is reported. The phenomenon is not due to an increase in total hydrocarbons from incomplete combustion. In fact, the total hydrocarbons are often decreased as more methyl esters are present in the fuel blends or when neat methyl ester fuels are compared to a neat petroleum diesel fuel. The mutagenicity usually associated with VO seems to be decreased by SME, even considering the larger quantities of VORG present.

Durability tests of 200 and 1000 hours duration have been performed using methyl ester diesel fuels with a variety of direct injection (DI) and indirect injection (IDI) diesel engines. High speed diesel engines have been shown to operate well for extended periods of time using methyl ester fuels and various combinations of methyl esters with number one and number two petroleum diesel fuels as long as the conversion of vegetable oil to esters is greater than 95%. Compatibility of materials might be an issue with methyl ester fuels. Esters with a high degree of unsaturation are excellent plasticizers and can degrade certain types of rubber components such as fuel lines and some types of fuel tank coatings. Nylon or Teflon coated fuel lines are necessary for extended operation using most types of methyl ester fuels. Difficulties with other fuel system elastomers have not been reported.

Fuel handling and storage safety might be improved by the use of methyl ester fuels. Methyl esters are biodegradable and much less toxic than diesel fuel. Methyl esters also have a much higher flashpoint than diesel fuel (180 degrees C versus 78 degrees C).

PRE-PROJECT WORK

Preliminary testing of neat SME (transesterified to 97% purity) fuel was conducted before this project began formally. The objective of the preliminary tests was to determine if SME combustion and emission characteristics in a mining diesel engine were favorable and worth a more thorough examination. Neat SME and #2 diesel fuel were tested using a 10-mode steadystate test on a Caterpillar 3304 indirect injection (IDI), naturally aspirated, diesel engine. DPM was reduced for several of the test modes when using SME, and was not significantly changed in other modes. The VORG was significantly increased and the NVOL fraction of the DPM was significantly decreased using SME. Gaseous hydrocarbons and CO were reduced and NOx was unchanged.

The results of the preliminary tests demonstrated that SME warranted extended testing to examine its ability to reduce diesel emissions, so a thorough test plan was developed. Other
research had indicated that SME could cause increases or decreases in NO\textsubscript{X} depending on the engine and conditions. Results of the preliminary testing with the Caterpillar IDI diesel engine showed no NO\textsubscript{X} increases, while combustion characteristics (ignition delay) and general operating performance showed only minor changes. The IDI type engines are used extensively in underground mining applications and were chosen for more comprehensive testing of SME.

Because steady-state tests and transient tests provide different insights into emissions characteristics, both types of tests were chosen for this test program. The ISO 8178 C-1 eight-mode test procedure was chosen for the steady-state testing. This test is designed for off-road engines and is a standard test that will allow for comparisons between laboratories. Two transient tests were chosen for the test program; a light-duty transient and a heavy-duty transient. These tests are unique to the USBM and were developed using load/speed modes that are similar to those observed during actual mine diesel operation. The two transients provide a further means of determining the performances of the SME fuel. The transient tests and the steady-state test are described in the methods section.

The preliminary tests showed that SME decreased the NVOL, but significantly increased the VORG portion of the DPM. To achieve significant DPM reductions when using SME, DOCs were included in the test program because they can reduce the volatile fraction of the exhaust by up to 50%. Two DOCs were chosen: a conventional formulation catalyst that has been previously tested by the USBM and an advanced formulation catalyst that was designed to minimize formation of sulfates and NO\textsubscript{2}.

Preliminary testing with non-distilled SME showed that quality control of the transesterified product was inconsistent. Most of the SME was 95 to 97% transesterified. However, some of the SME was significantly contaminated (>20%) with glycerine, free fatty acids, and unreacted triglycerides. This was probably due to settling during storage. Use of the contaminated SME fuel increased NO\textsubscript{X} emissions and prolonged use could have led to engine damage. Neat, distilled (>99% purity) SME from a single batch was chosen for the test program to control the quality of the SME for diesel fuel use. Commercially available low sulfur, #2 diesel fuel was chosen as a baseline fuel. Finally, a blend of these two fuels was considered to possibly be the most economically feasible fuel for mine use, and a blend was included in the test program. After testing both neat SME and #2 diesel fuel, a blend was chosen which, when used with a DOC, would provide a 30% to 40% reduction in total DPM. A blend of 30% neat SME and 70% D2 was chosen for as third test fuel.

Before undertaking the work of this contract the Bureau applied a previously developed technique for injecting liquids directly into the exhaust stream from the engine and observing the responses of various measurements. In particular, neat SME was injected and its alkane equivalent carbon number distribution (C#) was observed. This technique was calibrated by injecting a mixture of hexane and alkane C 18 which showed quantitative recovery of total C# 18 as DPM and XOC (vapor-phase material) within 30%. This is well within the absolute accuracy expected of the mass chromatographic analysis. The injection of SME showed an overwhelming two number spectrum at alkane equivalent C#s 19 and 21.

METHODS and APPARATUS
Tests were conducted on a CAT 3304 7 liter, naturally aspirated, IDI engine. This engine is rated at 75 kW at 37 Hz, with a peak torque of 380 N-m at 20 Revs/s, and is representative of engines used in underground mines. Figure 3 shows a schematic of the laboratory.

To maintain equivalent intake oxygen concentration in the presence of day-to-day variations in humidity and barometric pressure, the intake pressure was controlled while the intake temperature was maintained at 25 degrees C.

The engine and exhaust system were thoroughly conditioned after fuel changes. The fuel lines were drained and the new fuel was used for 8 hours at high exhaust temperature conditions (37 Revs/s and 305 N-m) before testing was performed. When the oil was changed, the engine and exhaust system were conditioned for 14 to 16 hours. The exhaust system conditioning was performed between the fuel and oil changes in order to limit the presence of residual, adsorbed volatile compounds in the exhaust system and combustion chamber from the testing of the previous fuel. However, it was noted in analyses that sulfates and phosphorus residuals were present even after this conditioning period.

The following is the test matrix that was used for both transient tests.

<table>
<thead>
<tr>
<th>Aftertreatment</th>
<th>#2 Diesel</th>
<th>Methyl Soyate</th>
<th>Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Conventional DOC</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Advanced DOC</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

The steady-state test matrix was as follows:

<table>
<thead>
<tr>
<th>Aftertreatment</th>
<th>#2 Diesel</th>
<th>Methyl Soyate</th>
<th>Blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>None</td>
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<tr>
<td>Conventional DOC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Advanced DOC</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
Three fuels were tested. The baseline diesel fuel was a commercially available low sulfur, number 2 petroleum diesel fuel (D2) from a single batch. The test fuels were distilled, neat SME and a blend of 30% SME by volume with 70% D2. The fuel related properties are given in table 1.

**Diesel Oxidation Catalyst Aftertreatment**

Two DOCs were used during the test program. An Engelhard advanced formulation DOC was used for both the steady-state and the transient portions of the emissions tests. The DOC was originally packaged specifically for our application, but is now commercially available under the name Bio-Cat. The DOC used a platinum and rare earth based technology. The monolith was approximately 24.1 cm in diameter, 7.6 cm long and had a cell density of 46.5 cells per square cm. Specific information about the catalyst washcoat formulation is proprietary, but the catalyst was designed by Engelhard to minimize oxidation of NO to NO₂, and SO₂ to sulfates, when compared to typical DOC formulations.

An older formulation Engelhard DOC was used for the transient portion of the testing. This DOC had a ceramic monolith, a cell density of 31 per square cm, and is commercially available under the name PTX-10. The older formulation DOC was not tested during the steady-state portion of the test program because it produced much more sulfates than the advanced formulation DOC.

**Fuel Injection Timing**

Preliminary testing by USBM and others found differences in the ignition delay and the NOₓ - particulate trade-off with changes in injection timing for SME and D2. Additionally, the stock injection timing of the Cat 3304 was not optimized from the standpoint of emissions with D2. A sweep of different injection timing settings was performed with both D2 and SME by running a light-duty transient test at four different injection timing settings: stock timing (13.5 °BTDC), 2° advanced (15.5 °BTDC), 2° to 2.5° retarded (11 to 11.5 °BTDC) and 3° to 3.5° retarded (10 to 10.5° BTDC). The Caterpillar 3304 PCNA uses fixed injection timing, which greatly simplified the process. A light-duty cycle was chosen to maximize NOₓ and volatile organic DPM emissions (the transient test is described in the methods section). DPM samples were collected at each condition with the partial-flow dilution tunnel. Gaseous emissions were also measured. Cylinder pressure measurements were taken at the rated speed and load to determine the ignition delay and rate of cylinder pressure rise. A fuel injection timing was chosen that took into account NOₓ, NO₂, and DPM emissions (primarily), as well as brake-specific fuel consumption, load response and rate of cylinder pressure rise (secondarily). Based on these criteria, a nominal injection timing of 10.5 to 11° was found to be optimum for both D2 and SME. The nominal injection timing was set to 10.5° BTDC for the remainder of the tests.

**Experimental Design**

The test program was designed to achieve coefficients of variation which would allow distinction between likely emissions differences. For the steady-state tests, four to five DPM samples were taken at each mode, and each test was repeated four times for each fuel and exhaust aftertreatment test condition (six repetitions for the D2 baseline). For the transient tests, 8 samples were taken for each transient type (light and heavy duty) and the tests were repeated four times for each test condition.
The test schedule varied the order of testing for the different fuels and the DOC, but was not random. Although a random test schedule would have been ideal, the schedule was compromised because of the time involved in oil and fuel changes and conditioning. Each fuel was tested with new oil and with older oil (more than 35 operating hours) to isolate differing lubrication oil effects on the DPM emissions. Statistical differences were analyzed using a two-sided t-test, with differences considered significant at P-value < 0.05.

Consistent DPM filter handling procedures provided small variations in DPM concentration determinations for the same test conditions. Data points were eliminated only if they could be attributed to known procedural errors or to mechanical engine faults that were not fuel related. For the steady-state tests, approximately 40 out of 950 DPM samples were eliminated.

**Transient Testing Methods**

**Test Cycles**

Two transient tests were chosen for the test program; a light-duty transient and a heavy-duty transient. These tests are unique to the USBM and were developed using load/speed modes that are similar to those seen during actual mine diesel operation. The transients consist of 16 load/speed segments, each 10 seconds long. This cycle lasts 160 seconds and is continuously repeated during a test. The light duty transient has a maximum load of 50% of the rated torque. The heavy duty transient has a maximum load of 90% of the rated torque. The heavy-duty transient was chosen because it was approximately the maximum load that could be attained by all fuels during the USBM test cycle. Figures 4 and 5 show the setpoints and actual response for heavy-duty transient test.

The transient tests were identical for all fuels. This was done to allow direct comparisons of brake specific emissions for different fuels doing identical work. However, only the emissions were compared, and the differences in equivalence ratio were not accounted for. Oil changes were done concurrently with each fuel change during the transient testing. This was done to minimize the effects of fuel diluted oil on the chemical composition of the DPM. However, by changing fuel and oil simultaneously, the effects of changing the lubricating oil on the emissions of the engine could not be differentiated.

**Emissions Measurement Equipment and Procedures**

Figure 3 shows a schematic of emissions measurement apparatus. Carbon monoxide (CO) and carbon dioxide (CO$_2$) were measured using nondispersive infrared (NDIR) analyzers, unburnt hydrocarbons were measured using flame-ionization detection (FID), and a chemiluminescence detector was used to measure NO. As a supplement to these conventional gas analyzers, a Fourier transform infrared (FT-IR) wide-spectrum analyzer was also used to measure other gas constituents. The FT-IR analyzer is capable of measuring many exhaust constituents in real-time including, CO, NO, NO$_2$, and various particular hydrocarbon species.

Diesel Particulate Matter (DPM) was collected using a partial-flow dilution tunnel (see Figure 3). The dilution tunnel, a positive displacement pump pulls clean, cool (approximately 20 degrees C) air through the dilution tunnel and through Pallflex 0.5m x 0.5m, Teflon-coated, glass-fiber filters. Raw exhaust is drawn through a sharp-edged orifice into the dilution tunnel, where it is diluted with clean air at dilution ratios of approximately 15:1 over a 5 m path and deposited on the filter. Exhaust backpressure was set to 4 kPa above atmospheric pressure at high idle for each test to help maintain adequate sample flow through the sharp-edged orifice. Sampling times typically varied from 16 to 30 minutes, and 300 mg of soot were targeted for each filter.
Eight to nine filter samples were taken for each transient test, and each test was repeated a minimum of four times. Also, an XAD-2 resin collector was used to sample vapor-phase hydrocarbons downstream of the DPM filter. One sample was collected per test, simultaneously with a DPM filter, and these were retained for solvent extraction and chemical and biological analysis. One DPM sample was also used for inorganic material analysis.

The partial-flow dilution tunnel incorporates a heater to minimize the variances in dilution tunnel and filter-face temperatures. The heater was turned off during the heavy-duty transient, during which the filter-face temperature averaged approximately 45 degrees C. The heater was set to 45 degrees C during the light-duty transient, allowing the filter-face temperature to be similar for both tests. Also, the dilution tunnel heater was used during engine conditioning periods. The exhaust system and dilution tunnel were conditioned by constantly taking DPM samples during the engine conditioning, with the dilution tunnel heater controlled at 45 degrees C. The conditioning was performed between the fuel changes to limit the presence of residual, adsorbed volatile compounds in the exhaust system, dilution tunnel, and combustion chamber from the testing of the previous fuel.

Gravimetric analysis was made of the DPM samples, and the volatile organic fraction was determined using vacuum-oven sublimation (at 200 degrees C). Chemical analysis was performed on selected samples to determine the sulfate and phosphorus fractions of the DPM. The exhaust opacity was also monitored in real time using a Celesco Model 107 light-extinction meter.

**Chemical and Biological Analysis of Samples**

Selected DPM and gas-phase material samples were analyzed at Michigan Technological University (MTU) for mutagenicity and \(n\)-alkane equivalent carbon number distribution. The samples were generated during the transient testing with the partial-flow dilution tunnel. Gas-phase material was collected in an XAD2 resin bed located downstream of the DPM sample. Soxhlet extraction was used to extract the organic material from the particulate filters and XAD2 resin, and carbon number distributions were determined using gas chromatography. Mutagenic activity was determined using the Ames mutagenicity bioassay.

Additional tests were performed to determine the gas chromatographic spectrum of emissions containing SME, and to determine the partition of the emissions between the soluble organic fraction of DPM and the gas-phase material. DPM and XAD2 samples were collected in the partial-flow dilution tunnel. The samples were analyzed at MTU for carbon number distribution for comparison with extractions of particulate and vapor phase organic material generated with SME fuel combustion without injection into the exhaust. The fatty acid composition of the SME used as fuel and for fuel blending is located in the appendix.

**Steady-State Methods**

Steady-state testing was conducted using the (ISO) 8178-C1 8-mode, off-highway test procedure (table 2). The only deviation from this procedure was the use of a non-standard exhaust backpressure which was necessary to allow for sampling with the BG-1 micro-dilution tunnel. The ISO test procedure calls for specific test points referenced to maximum torque at rated and intermediate speeds with an additional test point at idle. The intermediate speed is the maximum rated torque speed. Maximum torque at the rated and intermediate speeds was determined for each fuel tested at approximately the same equivalence ratios. The test points for each individual fuel were then referenced to these points:
Table 2. Setpoints for the ISO 8-mode steady-state tests

<table>
<thead>
<tr>
<th>Mode</th>
<th>Speed</th>
<th>Load</th>
<th>Same Equiv. Ratios</th>
<th>Weighting Factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Rated</td>
<td>100%</td>
<td>0.67</td>
<td>0.15</td>
</tr>
<tr>
<td>2</td>
<td>Rated</td>
<td>75%</td>
<td>0.52</td>
<td>0.15</td>
</tr>
<tr>
<td>3</td>
<td>Rated</td>
<td>50%</td>
<td>0.39</td>
<td>0.15</td>
</tr>
<tr>
<td>4</td>
<td>Rated</td>
<td>100%</td>
<td>0.21</td>
<td>0.10</td>
</tr>
<tr>
<td>5</td>
<td>Intermediate</td>
<td>100%</td>
<td>0.64</td>
<td>0.10</td>
</tr>
<tr>
<td>6</td>
<td>Intermediate</td>
<td>75%</td>
<td>0.46</td>
<td>0.10</td>
</tr>
<tr>
<td>7</td>
<td>Intermediate</td>
<td>50%</td>
<td>0.33</td>
<td>0.10</td>
</tr>
<tr>
<td>8</td>
<td>Low idle</td>
<td>0%</td>
<td>0.10</td>
<td>0.15</td>
</tr>
</tbody>
</table>

The engine timing settings were kept the same as for the transient testing (described above).

Cylinder Pressure Measurements

In-cylinder pressure measurements were used to determine the apparent heat release rates for each fuel tested at seven of the eight steady-state test modes (idle mode excluded). This provided a comparison of the combustion characteristics of the fuels tested. The cylinder pressure was measured using a quartz pressure transducer mounted in the engine's precombustion chamber with a separate charge amplifier. The combustion chamber of the tested engine contains a relatively large opening between the pre- and main combustion chambers, allowing the pressure measurements to correspond fairly well to main chamber events. However, it should be noted that since cylinder pressure measurements were not made in the main combustion chamber as well, the results are only useful as a relative comparison for this particular experiment. The start of fuel injection and the injection duration were determined through measurements of injection line pressure immediately upstream of the injection nozzle using a second quartz transducer and charge amplifier. A digital-storage oscilloscope was used for collection of cylinder and fuel pressure data. The oscilloscope was externally clocked and triggered by an optical encoder attached to the engine crankshaft and referenced to top dead center. Data were downloaded from the oscilloscope to a personal computer for reduction. The normalized apparent heat release rates were calculated using the single zone, Krieger-Borman model.

Size Distribution Measurements

Size distribution measurements were also made during the steady-state portion of testing. Aerosol size distribution measurements of neat SME, the blend fuel and D2 exhaust were made using a TSI Electrical Aerosol Analyzer (EAA). The EAA works on the principals of diffusion charging - mobility analysis, where the size distribution of a highly dilute exhaust aerosol is determined according to the particles' electrical mobility equivalent diameter. Others have used the EAA to measure diesel exhaust size distributions and the EAA has been found to have good correlation to other methods, such as diffusion battery / condensation nuclei counter combinations.

Diesel exhaust particles are usually less than 1 micron in diameter and often have a bi-modal distribution when observed immediately after leaving the exhaust manifold of an engine: a nuclei mode of very small particles (0.0075 to 0.056 um) and an accumulation mode (0.056 to 1.0 um). The nuclei mode is considered to be comprised of carbonaceous particles and nucleated, condensed hydrocarbons, and the accumulation mode particles are agglomerates of the carbon
particles with adsorbed hydrocarbons and sulfates. Diesel exhaust aerosol is less likely to show a bi-modal distribution far downstream of the engine, as particles have had time to agglomerate and grow. Particle size measurements were taken approximately 6 meters (~.5 second) downstream of the engine, so it is expected that the aerosol would retain some bi-modality.

The EAA exhaust samples were drawn from the dilution tunnel and further diluted prior to entering the EAA (figure 3). Diesel aerosol can be highly charged, so particles are first neutralized by passing through a Kr-85 neutralizer. The EAA measures 9 different size ranges less than 1 micron and outputs the particle concentrations at the mid-point diameters of the 9 size ranges. EAA data was reduced using the Simplex minimization curve fitting procedure.

Emissions Measurement Element and Procedures

For the steady-state ISO test procedure, DPM was collected using a Sierra BG-1 microdilution tunnel, a commercially available sampling system developed by Caterpillar and Sierra Instruments, Inc. This system meets the DPM measurement criteria set for the ISO-8178 test procedures. The BG-1 extracts a small fraction of the exhaust at a constant flowrate, dilutes the exhaust, and collects DPM on a 90 mm filter. Sampling times were typically two to eight minutes and sample masses of at least two mg net were targeted. Four to five samples were taken at each mode of each test. Exhaust backpressure was set at 1.2 kPa above atmospheric pressure at high idle for all tests. This backpressure condition deviated from ISO 8178 recommendations for exhaust backpressure, but was necessary to allow DPM sampling with our micro-dilution tunnel in our laboratory. DPM sample analysis was the same as for the transient tests.

Gas analyses were conducted in the same manner as during the transient testing (described above). Again, the exhaust opacity was also monitored in real time using a Celesco Model 107 light-extinction meter.

Chemical Analysis of Samples

Selected DPM filter samples have been analyzed for sulfate (SO₄) and phosphorus (P). This was done by dissolving the materials from DPM in hydrochloric acid and subsequent analysis by ion chromatography and mass spectrometry.

RESULTS and DISCUSSION

The following results are compared to the diesel fuel baseline with no DOC unless otherwise noted.

Transient

Diesel Particulate Matter Emissions

DPM results for the transient testing are shown in figures 6 and 7. The methyl ester fuels tended to decrease NVOL emissions and increase VORG emissions. These trends produced overall decreases in DPK with neat SNM decreasing by 30% for the heavy-duty transient and 23% for the light-duty transient. For SME in the heavy-duty transient, the VORG increased 37%, but was offset by a 57% decrease in NVOL. For SME in the
fight-duty transient, the VORG decreased 4% and the NVOL decreased 48%. The blend showed a decrease of 1% in total DPM for the heavy-duty transient, and no statistically significant difference for the light-duty transient.

The DOCs were generally able to reduce VORG emissions and cause decreases in total DPK although performance of the two DOCs was not similar. The conventional DOC was not as efficient as the advanced formulation DOC at reducing the volatile fraction of DPM. Also, the conventional DOC produces sulfates at high temperature conditions (the heavy-duty transient), causing total DPM to actually increase when used with D2. The advanced formulation DOC was efficient at reducing the VORG and provided decreases in total DPM with each fuel. The advanced DOC with SME fuel reduced total DPM by 65% and 64% for the heavy-duty and light-duty transients, respectively. With the blend fuel, the advanced DOC reduced total DPM by 35% and 4% for the heavy-duty and light-duty transients, respectively. The advanced DOC's performance with D2 was different than expected. For the heavy-duty transient, the advanced formulation DOC reduced NVOL considerably and was much more efficient at reducing VORG than it was in other cases. The result is a 50% decrease in DPM from using the advanced DOC with D2. This trend was not expected and has not been explained, but the trend was not repeated in the steady-state portion of the testing.

**Chemical and Biological Results**

Figure 8 is a C# spectrum of combined DPM and XAD2 materials collected when the engine was operating with SME fuel and no DOC present. It shows the conspicuous C# 19, 21 peaks previously identified as unaltered SNE fuel. This verifies that some SME is emitted by the engine without modification (usually called the unburned fuel constituent of exhaust). Hydrocarbons in diesel exhaust with equivalent carbon numbers above C16 are primarily adsorbed or condensed onto the DPM, and hydrocarbons with smaller chain lengths are primarily collected as gas phase material. Longer chain hydrocarbons that are predominantly adsorbed and condensed to the DPM as VORG are usually associated with incomplete combustion of lubricating oil, which has alkane equivalent carbon numbers ranging from about C14 to C30.

If longer chain, higher boiling point, fuel related organic compounds remain intact at the end of combustion of SME, the increased level of DPM adsorption for these species could account for the increase in VORG with a simultaneous decrease in the total vapor-phase hydrocarbons. The C19 and C21 peaks that were observed during emissions analysis (no injections) constitute 60% of the mass of the total DPM and hydrocarbon emissions. The C19 and C21 constituents were responsible for 80% of the organic material extracted from the DPM and 47% of the vapor phase organic material. Further analysis is necessary to determine the exact composition of these organic compounds, but the results from the injection tests strongly suggest that the C19 and C21 components are fuel related and are probably methyl esters emitted with little or no chemical change.

The mutagenic activity of a limited number of DPM and gas-phase samples was determined. The principal mutagenicity results were:

The mutagenicity of the DPM (revertants/kg-exhaust) when SME fuel is used with the advanced DOC is about half that when D2 is used with the advanced DOC.

The mutagenicity of the DPM emitted with SME fuel and the DOC is about 40% of that without the DOC.
The mutagenicity of the gas-phase portion of the emissions is negligible when SME fuel is used with a DOC.

The reduction in mutagenic activity when using SME is probably a result of reduced PAH emissions due to the lack of fuel PAH. Similar results have been found in other research. Further chemical analysis with speciation of the extracted organic material will be necessary to understand the observed reduction in mutagenic activity.

**Gaseous Emissions**

Gaseous emissions trends showed decreases or no significant increases for all of the major exhaust pollutants. NO\textsubscript{x} was reduced for both the blend fuel and the neat SME fuel by 10\% to 11\% for both transients. Combustion analyses that show a decrease in the pre-mixed burn phase of combustion, lower peak bulk gas temperatures, and decreased ignition delay may contribute to the explanation for these decreases, and are described in later sections.

CO was reduced significantly with both the blend fuel and the SME fuel. Neat SME reduced CO levels by 23\% for both transients, and the blend showed decreases of 19\% and 23\% for the light-duty and heavy-duty tests, respectively. FID-hydrocarbons were decreased by 36\% and 33\% for the SME fuel and 25\% and 24\% with the blend fuel for the light-duty and heavy-duty tests. Formaldehyde showed slight decreases with the methyl ester fuels, but the only statistically significant decreases occurred for neat SME during the light-duty transient and for the blend during the heavy-duty transient. NO\textsubscript{2} showed statistically significant increases for the neat SME fuel during both transients, although all NO\textsubscript{2} measurements without the DOCs were very low (< 12 ppm).

Both DOCs had similar performance, except the conventional formulation DOC produced significant amounts of NO\textsubscript{2} when used with both D2 and neat SME fuels. For the light-duty transient, the conventional DOC with D2 reduced FID-HCs by 64\% and CO by 86\%, and the advanced DOC with D2 reduced FID-HCs by 60\% and CO by 76\%, compared to the D2 baseline. For the heavy-duty transient, the conventional DOC with D2 reduced FID-HCs by 73\% and CO by 82\%, and the advanced DOC with D2 reduced FID-HCs by 82\% and CO by 84\%, compared to the D2 baseline.

DOC performance with the methyl ester fuels was similar to the performance with D2, providing overall decreases compared to the D2 baseline of 70\% to 90\% for FID-HCs and CO. Formaldehyde was significantly decreased using the DOCs. NO\textsubscript{2} increased during the heavy-duty transient for both DOCS. The conventional DOC increased NO\textsubscript{2} during the heavy-duty transient by 11 and 20 times for the D2 and the neat SME fuels, respectively, and also increased NO\textsubscript{2} for the light-duty transient. The advanced formulation DOC decreased NO\textsubscript{2} for the light-duty transients, but increased NO\textsubscript{2} for the heavy-duty transients. NO\textsubscript{2} values were low (< 20 ppm) for all tests. Summaries of gas data for both transients are tabulated in the appendix.

**Steady-State**

**Diesel Particulate Matter Emissions**

ISO Weighted Average Results:

Figure 9 shows the weighted average results for total DPM emissions and the
contributions of both VORG and NVOL components of the DPM over the ISO 8178-C1 steady state test procedure. The error bars refer to standard errors (propagated for a total uncertainty) for total DPM. Compared to the D2 baseline, all other cases showed statistically significant decreases except the 30/70 blend with no DOC. Neat SME decreased total DPM by about 31%. Both SME and the blend had substantially greater VORG emissions, but the NVOL DPM constituents (carbonaceous soot) were significantly reduced, resulting in overall DPM reductions. The DOC was very effective in reducing the VORG and total DPM over the ISO test procedure. When the DOC was used with D2, VORG was reduced by 43% and total DPM was reduced 19%. The DOC combined with the blend resulted in total DPM reductions of 35%, and with neat SME resulted in reductions of 59% when compared to D2. Also notable is a 49% reduction in total DPM when SME with a DOC is compared to D2 with a DOC. Exhaust opacities were generally low (<5%), the opacity values correlated well with the gravimetrically determined nonvolatile fraction of DPM.

Results for Particular Modes:

Typical, non-weighted brake specific DPM emissions are shown for a heavy load and a light load at the rated speed (37 Revs/s), and for an intermediate load and speed in figures 10, 11, and 12. The error bars refer to standard errors. Note that figure 9 has a different scale because it is a low power mode. The contribution of VORG to total DPM increases with decreasing speed and load for all modes shown. At the low load condition, the increase in VORG for the 30/70 blend without the DOC resulted in no net change in total DPM emissions when compared to the baseline D2 case. The same is true for neat SME and the 30/70 blend at the intermediate speed and load condition. The DOC reduced VORG and total DPM except for the case of D2 and the 30/70 fuel blend at the high speed high load condition. Although the D2 fuel tested and used as a base for the 30/70 blend is a low sulfur (<0.05 mass%) fuel, the sulfur content was sufficient to allow significant formation of sulfate compounds by the DOC at conditions with high exhaust temperatures. This contributed to a net increase in DPM levels when the DOC was used with the petroleum fuel and the 30/70 blend, but only at the rated speed, 100% load condition (mode 1).

Gaseous Emissions

Gaseous emissions results show a decrease of several exhaust gas emissions species for neat SME compared to the D2 baseline fuel. No statistically significant increases occur for any of the observed exhaust gases. Results from the 30/70 blend show smaller decreases. Tables 3 and 4 show ISO-weighted average results for several exhaust gas species for each fuel and aftertreatment tested. Asterisks denote statistically significant differences (P<0.05) between fuel or fuel and DOC conditions. No significant difference in gaseous emissions trends was noted between the ISO-weighted average results and the transient test cycle results. The neat SME fuel showed a statistically significant reduction in NO\textsubscript{x} emissions when compared to the D2 baseline, but none of the other conditions were significantly different than D2. Other investigations of oxygenated diesel fuels have shown that a decrease in NO\textsubscript{x} emissions is possible if ignition delays are shortened. Results from this and other investigations indicate that the NO\textsubscript{x} change could partially be explained by decreased ignition delays and reductions in the pre-mixed burn phase of combustion.

Weighted-average brake specific emissions of FID-HCs were reduced by 24% when using neat SME, but BSCO showed no decrease. When using the blend, FID-HCs were reduced by 18% and BSCO was reduced slightly (6%, not significant). The reductions in gas-phase hydrocarbons may be explained by the carbon number distribution, as discussed above. Emissions of N0\textsubscript{2} were increased when using neat SME, although
concentrations were low and near the limit of detection for the FT-IR analyzer. Formaldehyde emissions were not significantly affected by either the neat SME or the blend. Emissions of \( \text{SO}_2 \) were very low for all conditions.

The DOC did not affect \( \text{NO}_x \) or \( \text{NO} \). When the DOC was used with neat SNE, BSCO was reduced by 74\%, BSHCs by 76\%, and formaldehyde by about 26\% (although all concentrations of formaldehyde were very low and near the detection limit of the FT-IR analyzer). The DOC in combination with neat SME did increase \( \text{NO}_2 \) emissions further, but all \( \text{NO}_2 \) concentrations were less than 10 ppm. When the DOC was used in conjunction with the blend fuel, BSCO was reduced by 69\% and BSHCs were decreased by 75\%, with no significant increase in \( \text{NO}_2 \). When the DOC was used with D2, BSCO emissions were decreased by 69\% and BSHCs were decreased by 72\% when compared to the D2 baseline.

Gaseous emissions trends for the transient tests correlated well with the ISO steady-state weighted average results.

Gaseous emissions trends for individual modes of the eight-mode test were similar to overall trends. Figures 14, and 15 show \( \text{NO}_x \) emissions for Modes 1, 4, and 6, respectively. Error bars refer to standard errors. Note that the scale on figure 12 is different because it is a lower power mode. Although \( \text{NO}_x \) trends were consistent, the differences between modes can be explained in-part by the differences in combustion events (described below). \( \text{NO}_x \) decreases using SME were greatest at partial load.

**Sulfate**

Approximately half of the total \( \text{SO}_4 \) was found to be non-volatile in the sense that it remains on the filter after vacuum sublimation. The implication of this finding is that whenever appreciable sulfate is present (i.e. fuels containing appreciable amounts of sulfur), half of its concentration should be subtracted from the volatile constituent of DPM to yield VORG and half subtracted from the nonvolatile constituent to yield NVOLC (non volatile carbon).

All concentrations of \( \text{SO}_4 \) are reported as doubly hydrated \( \text{SO}_4 \) because previous experience has indicated that this is the equivalent form in which it appears during routine gravimetric analysis. Up to 10 mg/kg of \( \text{SO}_4 \) were emitted in modes 1 and 5 when diesel fuel and a DOC were used. About half this concentration appears when the 30/70 blend is used. No significant \( \text{SO}_4 \) is found in other cases.

A severe limitation in our ability to quantify the \( \text{SO}_4 \) emitted during these tests is imposed by the tendency of \( \text{SO}_4 \) to be retained in the exhaust and measuring systems beyond the conditioning times that are routinely allowed between tests, particularly when fuel is changed. For example, modes 1 and 5 show up to 2 mg/kg \( \text{SO}_4 \) when SME fuel is used for the first tests of SME after D2. This is believed to be an artifact caused by retention of \( \text{SO}_4 \) in the DOC and subsequent reemission when high exhaust temperatures are encountered.

**Phosphorus**

Approximately 0.1 mg/kg of phosphorus (P) is observed in mode 5 when the fuel is D2 and no DOC is present. About half this concentration is found in mode 5 when the DOC is used and in mode 1 whether the DOC is present or not. About 0.05 mg/kg P is also apparent in mode 5 when the fuel is a blend or SME. Other modes show smaller concentrations of P.

It is believed that the P arises from lube oil. The budget of lube oil consumed
approximately balances with the magnitude of concentrations found in the DPM. The problem of the measurement limitations likely imposed by retention and subsequent reemission of P by the sampling and instrumentation system is probably present by analogy with the definite problem cited above for SO$_4$.

**Combustion Analysis**

Heat Release Rate: Figures 16, 17 and 18 show the normalized apparent heat release rates (AHRR) for three representative test conditions. The two peak heat release rates normally associated with premixed and diffusion combustion are clearly evident. There was a significant decrease in ignition delay measured for the neat SME fuel and a smaller decrease in ignition delay for the 30/70 blend when compared to the D2 baseline fuel. Premixed bum fractions were reduced at the rated speed and partial to light loads for SME. The premixed bum fraction for SME was reduced significantly (32 vs. 53%) at the rated speed, light load test condition (figure 17), but NO$_x$ emissions were only slightly reduced. The premixed bum fraction for SME increased steadily with load until it was roughly equivalent with D2 at the rated speed, full load test condition (figure 16). The diffusion burn peak was slightly increased for SME at higher loads at rated speed, but was very similar for the other test conditions. No real inferences can be made about the end of combustion with the heat release data that is presented. The premixed burn fraction for the blend was somewhat higher than for the D2 baseline fuel at the intermediate speed test conditions, but was roughly equivalent for most test conditions at rated speed. There was a consistent, but statistically insignificant increase in NO and NO$_x$ emissions for the fuel blend that may have been a result of this phenomenon.

Peak Bulk Gas Temperature:

The peak bulk gas temperatures were reduced by SME and, to a lesser extent, by the blend, compared to the D2 baseline at all of the speed and load conditions. An example is shown in figure 19 (25 Revs/s). This is due primarily to the lower energy content of SME and the 30/70 SME/D2 blend. The similarity in the premixed burn fractions between SME and the D2 baseline are inconsistent with the observed NO$_x$ decrease with SME. The formation of NO is primarily temperature dependent. It is possible that the reduced peak bulk gas temperatures may be responsible for the reduction in NO$_x$ emissions with SME. It is important to note, however, that the transient tests gave practically identical NO$_x$ reductions for SME as the weighted average steady state ISO tests. The transient test cycle compared the fuels on a similar equivalence ratio basis that effectively lowered engine output (and bulk gas temperatures) for SME and the fuel blend.

Cumulative Burning Rates:

The cumulative burning rates for the three fuels show a trend towards release of fuel energy earlier in the cycle for the SME and to a lesser extent for the blend, but only at the rated speed and load condition (figure 20). Except for differences in early combustion events, the cumulative heat release at other test conditions is similar overall between the different fuels within the limitations of the heat release model that was applied (figure 21).

**Particle Size Measurements**
Particle size parameters calculated from EAA data are presented in table 5. The particle size distribution of DPM is bi-modal, consisting of a nuclei mode with a volume mean diameter typically between 0.0075 to 0.03 um, and an accumulation mode with a volume mean diameter typically between 0.1 and 0.4 um

Number and volume particle size distributions for each of the fuels and two steady state operating conditions are shown in the appendix. The number and volume distributions were quite similar for each of the fuels tested. At the 100% load condition, the number and volume distributions shifted from the accumulation mode to the nuclei mode for SME when compared to the D2 baseline. At the 10% load condition, the number and volume of particles in the accumulation mode were reduced for SNE, similar to the 100% load condition without a significant increase in smaller particles. The reduction in larger particles within the accumulation mode is also apparent from the differences in number and volume mean particle diameters for SME and D2 for that mode. No significant differences were found for the particle size distributions for the 30/70 blend when compared to D2. The differences in the particle size distribution near the 0.75 um midpoint cannot be considered significant due to the reduced accuracy of the EAA in the 0.75 to 1.0 um size range.

**Power and Fuel Consumption**

The lower energy content in neat SNM fuel resulted in lower power output and higher fuel consumption when compared to the D2 baseline fuel. At the rated speed and maximum torque condition, neat SME fuel produced only 91% as much power as D2 (71.3 kW to 78.3 kW). The blend produced approximately 96% of the power (75.6 kW).

Brake-specific fuel consumption increased with the use of SME fuel. Weighted-average brake-specific consumption for the steady-state testing was up 13.7% when using neat SME, and 3.8% when using the blend.

**CONCLUSIONS**

1. The SME fuel and the 30/70 blend fuel did not cause any fuel-related problems in the prechamber, naturally aspirated engine.

2. Neat SME and the 30/70 blend fuels increased the volatile organic fraction of DPM and decreased the non-volatile (carbonaceous soot) fraction when compared to D2. Overall, this resulted in a 31% decrease in total DPM for the neat SME during the steady-state testing, and 23% and 30% decreases for the light-duty and heavy-duty transients, respectively.

3. The volatile increase was primarily due to a to a higher carbon number for the volatile organic material for SME, shifting more of it into the adsorbed and condensed particulate phase and less into the vapor phase.

4. Extracts of particulate and vapor phase organic material were found to be significantly less mutagenic for SME when compare to D2.

5. Gaseous emissions of FID-HCs were reduced using both the 30/70 blend fuel and neat SME. Formaldehyde emissions were the same for all fuels.
NO\textsubscript{x} was not increased with the use of the 30/70 blend fuel and was decreased slightly with the neat SME fuel in the steady-state tests. For both transient tests, NO\textsubscript{x} was decreased approximately 10% for the neat SME fuel and the blend fuel.

The DOC decreased total DPM, CO, and FID-HC emissions. The advanced DOC reduced formaldehyde but caused a slight increase in NO\textsubscript{2} emissions when used with neat SME. Both formaldehyde and NO\textsubscript{2} emissions were very low in all cases.

The advanced formulation DOC performed better than the conventional formulation DOC. Both catalysts reduced CO and FID-hydrocarbons by similar amounts (60 to 90%, depending on the case), but the conventional formulation catalyst produced sulfates at high temperatures, was not as good at reducing the volatile fraction of the exhaust, and caused increases in NO\textsubscript{2} in some cases.

Size distribution measurements show a slight shift in the size distribution of the SME exhaust particles from the accumulation mode (larger particles) to the nuclei mode for some conditions. Further research is needed to determine the extent of the size distribution shift and the mechanism that could be causing it.

For the steady-state tests, the combination of SME with the advanced DOC reduced total DPM emissions by 59% compared to D2 with no DOC and by 49% compared to D2 with the advanced DOC. The combination of the 30/70 blend with the advanced DOC reduced total DPM emissions by 35% compared to D2 with no DOC and by 20% compared to D2 with the advance DOC. For the steady-state tests, neat SME combined with the advanced DOC reduced total DPM emissions by 65% and 64% for the heavy-duty and light-duty transients, respectively. The combination of the 30/70 blend with the advanced DOC reduced total DPM emissions by 35% and 40% for the heavy-duty and light-duty transients, respectively.

Overall combustion characteristics were quite similar for all of the fuels tested, with a tendency towards a reduction in the ignition delay for SME and to a lesser extent for the 30/70 blend. The shorter ignition delays contributed to reductions in the premixed burn fraction of combustion for SME at partial to light loads at the rated and intermediate speeds, which may be partially responsible for the observed NO\textsubscript{x} reductions.

Neat SME had 9% less power and 13.7% greater brake specific fuel consumption than D2. The blend produced 4% less power and had 3.8% greater brake specific fuel consumption.

Neat SME or a 30/70 blend, combined with an appropriate DOC, could potentially be used as emissions reduction technologies for confined space diesel usage, such as in underground mines. The reduced emissions from these fuels, along with increased biodegradability and higher flash points, could provide safety and health improvements over diesel fuel.
GLOSSARY

ADV - The advanced formulation diesel oxidation catalyst
AHRR - Apparent heat release rate: the estimated rate of heat release during combustion
Blend - 30% SME blended with 70% D2 by volume
Brake Specific - (Mass flow) divided by (brake power)
CI - Compression ignition
CONV - The conventional or older formulation diesel oxidation catalyst
D2 - Commercial, #2 diesel fuel from a single batch
DOC - Diesel oxidation catalyst
DPM - Diesel Particulate Matter (VORG + NVOL)
EAA - Electrical Aerosol Analyzer: for measuring particle size distribution
FID - Flame ionization detector: standard measurement method for total hydrocarbon emissions
FT-IR - Fourier transform infra-red analyzer: used for exhaust gas speciation
ISO - International Organization for Standardization
NVOL - The nonvolatile (carbonaceous) solid fraction associated with DPM
SME - Soy methyl esters
Standard Error - (Standard deviation) divided by (n)^1/2
VORG - The volatile organic fraction associated with DPM
XAD2 - An absorbent polymer used for the collection of vapor phase organic material