#### EXHAUST EMISSIONS AND PERFORMANCE OF DIESEL ENGINES WITH BIODIESEL FUELS

Christopher A. Sharp Southwest Research Institute

#### ABSTRACT

The use of biodiesel fuels derived from vegetable oils or animal fats as a substitute for conventional petroleum fuel in diesel engines is receiving an increasing amount of attention. This interest is based on a number of properties of biodiesel including the fact that it is produced from a renewable resource, its biodegradability, and its potential to reduce exhaust emissions. Transient exhaust emissions from three modern diesel engines were measured during this study, both with and without an oxidation catalyst. Emissions were characterized with neat biodiesel and with a blend of biodiesel and conventional diesel fuel. Regulated emissions and performance data were generated, and a detailed chemical characterization of exhaust emissions was performed.

The use of biodiesel resulted in lower emissions of unburned hydrocarbons, carbon monoxide, and particulate matter, with some increase in emissions of oxides of nitrogen on some engines. Biodiesel also increased catalytic converter efficiency in reducing particulate emissions. Chemical characterization also revealed lower levels of some toxic and reactive hydrocarbon species when biodiesel fuels were used. In addition, emissions of carcinogenic PAH and nitro-PAH compounds were substantially lower with biodiesel, as compared to conventional diesel fuel.

#### INTRODUCTION

As part of the Clean Air Act Amendments enacted by the U.S. Congress in 1990, under section 211(b), the U.S. EPA was directed to insure that any new commercially available motor vehicle fuels or fuel additives would not present an increased health risk to the public. Under this directive, EPA established a fuel and fuel additive registration program including a set of testing protocols, given in CFR Title 40 Part 79. These tests are designed to provide sufficient data for EPA to assess the impact of a given fuel or additive on the potential health risks posed by motor vehicle exhaust. The test protocols include a detailed characterization of the exhaust emissions of one or more engines while operating with the fuel or additive in question.

Biodiesel is proceeding as a commercial fuel in the U.S., and therefore it is required to meet the registration requirements described above. In addition, although considerable data is available on the effect of biodiesel on EPA regulated pollutants (i.e., HC, CO,  $NO_x$ , and particulates), most of this data was generated using older technology engines. Further, very little detailed exhaust characterization data on

biodiesel beyond the regulated pollutants exists.

In order to address these needs, the National Biodiesel Board (NBB) initiated a test program at Southwest Research Institute (SwRI) involving a detailed characterization of both regulated and unregulated exhaust emissions from current technology engines, operating on both biodiesel and conventional diesel fuel.

# **TEST DESCRIPTION**

# **Test Engines**

Three different test engines were employed during this test program, as summarized below in Table 1. These engines represented a wide range of potential applications for biodiesel fuel.

Engine	Rated Power, kw	Application		
1997 Cummins N14	276	Highway Truck		
1997 DDC Series 50	205	Urban Transit Bus		
1995 Cummins B5.9	119	Full-Size Pickup Truck		

**TABLE 1. TEST ENGINES** 

All three test engines were direct injected, turbocharged, and intercooled. The Cummins N14 and DDC Series 50 engines were electronically controlled, and both employed a fuel system incorporating high pressure electronic unit fuel injectors. The Cummins B5.9 engine, in contrast, was mechanically controlled, and used a pump-line-nozzle type fuel system which employed a Bosch inline injection pump. This difference in fuel injection between the B5.9 engine and the other two engines likely resulted in several differing trends in the emissions responses to biodiesel fuel.

Both the Series 50 and B5.9 engines normally employed a catalytic converter, while the N14 engine did not. The catalytic converters were oxidation catalysts, used primarily for the purpose of reducing particulate emissions. For the Series 50 and B5.9 engines, tests were run both with and without catalyst.

The N14 and Series 50 engines were new engines, and each was run 125 hours using neat biodiesel for break-in. The B5.9 engine had been used for previous biodiesel testing, and therefore did not require break-in.

# **Test Fuels**

Three test fuels were used during this program, including a neat (100%) biodiesel fuel, a neat (100%) diesel fuel, and a blend of 20 percent biodiesel by volume in the diesel fuel. Selected properties for all three fuels are given in Table 2.

The biodiesel fuel was supplied by Ag Environmental Products, and is referred to as "B100." The fuel was delivered via tanker to SwRI, and stored in an underground tank which was cleaned and rinsed with fuel from the same batch as the test fuel prior to the introduction of biodiesel. New test cell fuel systems were used to prevent contamination of the biodiesel fuel stream in route to the engine.

The diesel fuel for this program came from a batch specially blended in order to meet the stringent specifications required by the 211(b) regulations, as outlined in CFR 40 Part 79. This fuel is referred to in this report as "2D." The fuel was delivered to SwRI in 55 gallon drums.

The blended fuel was mixed at SwRI in several 55 gallon drums. The blend ratio was 20 percent biodiesel to 80 percent diesel fuel by volume. The blended fuel is referred to as "B20."

### **Test Procedures**

Transient Testing and Regulated Emissions Measurement

Exhaust emission characterization was performed as specified under CFR Title 40, Part 79. For heavy-duty engines, the regulation specifies that emissions are to be measured over the U. S. EPA heavy-duty transient Federal Test Procedure (FTP), as outlined in CFR Title 40, Part 86, Subpart N. The FTP outlines specific requirements for setting up the test engine and mapping the engine's full torque capabilities over its operating speed range. Engine-specific performance data are used, along with a normalized EPA transient cycle, to define a transient command cycle for test engine operation.

While the engine is operated over the 20-minute test cycle, torque and speed responses of the engine are compared to the command cycle to ensure FTP compliance. Simultaneously, engine exhaust gases are diluted with conditioned air, and emissions of interest are determined. Work generated by the engine is also recorded during the cycle. The FTP specifies both a cold-start test cycle (following an overnight soak) and a hot-start test cycle, with a 20-minute soak between the two test cycles. Measured emission masses for both cycles are weighted to produce a composite mass of oneseventh cold-start mass and six-sevenths hot-start mass. This composite mass is divided by a similarly weighted composite work to generate a brake-specific emission value in terms of mass of pollutant per unit of work generated.

# TABLE 2. SELECTED TEST FUEL PROPERTIES

Fuel	Riadianal Crass	B100	211(b)	00	Doo			
SwRI Fuel Code	Biodiesel Spec		Diesel Spec	2D	B20			
		EM-2481-F		EM-2494-F	EM-2532-F			
Cetane Number, D-613	40 min.	47.5	43.2-47.2	43.3	46.0			
Cetane Index		n/a	43.7-47.7	45.2	n/a			
Distillation, D-4052, °C								
IBP		331		192	196			
10%		333	221-227	226	234			
50%		336	266-272	266	285			
90%		341	316-322	321	337			
EBP		342		352	353			
API Gravity, D-4052		28.2	32-34	33.8	32.7			
Specific Gravity, D-4052		0.886		0.856	0.862			
Flashpoint, D-93, °C	100 min.	146		62	90			
Viscosity, D-445, cSt	1.9-6.0	4.12		2.80	2.92			
Sulfur, D-2662, wt%	0.05 max.	0.0000	0.0475-0.0525	0.0476	0.0370			
Carbon, D-5291, wt%		77.3		86.9	85.1			
Hydrogen, D-5291, wt%		11.8		13.1	12.6			
Oxygen, difference, wt%		11.0		n/a	2.1			
Aromatics, FIA, wt%	n/a	n/a	35.7-41.1	39.1	n/a			
Olefins, wt%	n/a	n/a	1.1-1.9	1.7	n/a			
Saturates, wt%	n/a	n/a	58.1-62.1	59.2	n/a			
Heat of Comb., D-240								
Gross, MJ/kg	_	39.8		45.3	44.0			
Net, MJ/kg	_	37.2		44.0	41.4			
Sulfated Ash, D-874	0.02 max.	0.001		0.001	<0.001			
Carbon Residue, D-189	0.05 max.	0.00		0.00	0.00			
Cloud Point, D-2500, °C		-1		-17	-14			
Pour Point, D-97, °C		-3		-21	-15			
Acid Number, D-664	0.80 max.	0.21		<0.005	0.05			
Water and Sediment, D-1796	0.05 max.	<0.02		<0.05	<0.02			
Copper Strip Corrosion, D-130	No. 3 max.	1A		1A	1A			
Total Glycerine, wt%	0.24 max.	0.19		n/a	0.04ª			
Free Glycerine, wt%	0.02 max.	0.01		n/a	<0.01ª			
a Calculated								

Regulated emissions measured during this program included total hydrocarbons (HC), carbon monoxide (CO), oxides of nitrogen (NO<sub>x</sub>), and particulate matter (PM). Hydrocarbons were measured using continuous sampling techniques employing a heated flame ionization detector (HFID). CO and  $CO_2$ , were determined using proportional dilute gaseous samples analyzed using non-dispersive infrared (NDIR) instruments. NO<sub>x</sub> was measured continuously during the transient cycle via an NO, chemiluminescence instrument. Total PM levels were determined by collecting particulate matter on a set of 90mm Pallflex (T60A20) filters which were weighed both before and after the transient test.

Regulated emissions were measured over the cold-start cycle and the first two hot-start cycles, but composite values were generated using only the cold-start and the first hot-start as specified by the FTP. In addition to the cold-start and hot-start typically used to compute the transient FTP composite, additional runs were made to accumulate sufficient sample for the reliable detection of semivolatile polycyclic aromatic hydrocarbons (PAH) at levels required by EPA. For the Cummins N14 engine, sample was accumulated in a single set of semivolatile PAH sampling media over one cold-start and six successive hot-starts (in order to preserve the one-seventh/six sevenths cold-hot FTP weighting). For the other two engines, semivolatile PAH sampling rates so that the portion of cold sample and hot sample was one seventh and six sevenths, respectively.

In an effort to prevent carryover in the sampling systems from one engine to the next, a preconditioning process was run when each engine was installed, prior to the start of testing. The engine was operated at maximum power for two hours with all sampling systems running. Subsequently, a torque-map was run, followed by six successive transient cycles, again with all sampling systems running. The engines were fueled on B100 for this preconditioning procedure.

Particulate Characterization

Particulate samples from the cold-start and the first two hot-starts were analyzed to determine the general composition of the particulate emissions by several methods. Filter samples were analyzed for soluble organic fraction (SOF) via a Soxhlet extraction method using a 30-70 mixture of toluene and ethanol as the solvent. Volatile organic fraction (VOF) was also determined using direct filter injection gas chromatography (DFI/GC). Finally, sulfate levels were determined via an ion chromatograph. All of these analyses were performed on sections of the particulate laden 90mm Pallflex filter pair from the selected runs. As with the regulated emissions, composite values for SOF, VOF, and sulfate were generated using only the cold-start and the first hot-start as specified by the FTP.

#### $C_1$ to $C_{12}$ , Hydrocarbon Speciation

Hydrocarbon emissions from  $C_1$  to  $C_{12}$  including aldehydes, ketones, and alcohols, were measured during this program. These analyses were performed on samples from the cold-start and the first hot-start only. Gaseous hydrocarbons from  $C_1$  to  $C_{12}$  except for aldehydes and ketones, were determined by analyzing proportional bag samples of dilute exhaust using a series of gas chromatographs, each optimized for a different carbon number range. The methods used for this analysis were the same as those developed for Phase II of the Auto Oil Program.<sup>1</sup>

Aldehydes and ketones from  $C_1$  to  $C_8$  were sampled and analyzed using a 2,4-dinitrophenylhydrazine (DNPH) technique outlined in CFR 40, Part 86, Subpart N for methanol engines.

#### PAH and nPAH Measurement

PAH and nPAH emissions were sampled in both the particulate phase and semivolatile phase. Particulate samples were obtained using a second, larger secondary dilution tunnel, to allow for the use of 20x20-inch Pallflex (T60A20) sampling media. This larger media size was necessary in order to obtain sufficient sample to meet EPA detection requirements for PAH and nPAH compounds. Background PAH/nPAH samples were obtained by operating the sampling systems with sampling media loaded, but without the engine operating, for 2 hours in order to obtain sufficient volume.

Semivolatile PAH and nPAH samples presented a particular problem, in that conventional sampling techniques would not allow for sufficient sample to be gathered to meet EPA detection requirements. Commercially available sampling media and hardware were of insufficient size to allow for the volume flow rates needed. However, even with custom built sampling hardware, the maximum sampling media size was also limited by the ability to extract and concentrate samples obtained. Therefore, an approach was devised involving both custom built sampling hardware and a modified sampling plan. The modified plan involved running multiple tests with a single set of sampling media, as was already described in paragraph 3 of this section.

The final sampling hardware setup for semivolatile PAH and nPAH emissions consisted of a pair of sample cartridges (rather than the usual single cartridge) operated in parallel and mounted on the larger secondary dilution tunnel, downstream of the  $20 \times 20$ - inch filter media used for particulate phase sampling. These cartridges

<sup>&</sup>lt;sup>1</sup>Siegl, W.O., Richert, J.F.O., Jensen, T.E., Schuetzle, D., Swarin, S.J., Loo, J.F., Prostak, A., Nagy, D., and Schlenker, A.M., "Improved Emissions Speciation Methodology for Phase II of the Auto-Oil Air Quality Improvement Research Program - Hydrocarbons and Oxygenates," SAE Paper 930142, Special Publication SP-1000.

were sized to allow a media diameter of 4 inches, rather than the conventional 2.5 inches. This larger diameter allowed a much higher flow rate to be used, while maintaining the face velocity within recommended levels for the sampling media. The sample cartridges contained a layered sampling media consisting of a 1.25 inch deep layer of polyurethane foam (PUF), a 0.5 inch deep layer of XAD-2 resin, and a second 1.25 inch deep layer of PUF. The XAD-2 resin was incorporated to improve the trapping efficiency for nPAH compounds, which were potentially present in much lower levels than PAH compounds.

After testing, sample sets were Soxhlet extracted for 16 to 18 hours. In cases where immediate extraction was not possible, samples were sealed and stored at 4°C. After extraction, the sample extracts were cleaned up by an acid wash and elution through a column packed with activated silica gel. After cleanup, the samples were analyzed using several high resolution gas chromatograph/mass spectrometer (GC/MS) instruments. For each analysis, a 1µL aliquot of the sample extract was injected into the instrument. For quantitation, an internal standard solution, made up of several deuterated PAH or nPAH compounds, was spiked into the extract at the time of analysis, and was used for calculating response factors.

Heavy Hydrocarbon (GC/MS) Speciation

The heavier hydrocarbons were sampled onto solid sorbent tubes which used a Tenax GRc sorbent medium, because they do not remain in the gaseous state at room temperature. Samples were obtained during the cold-start and the first two hot-starts, but only samples from the cold-start and the first hot-start were analyzed. At the time of analysis, the sorbent tubes were thermally desorbed by heating the tubes to 300°C while passing an inert gas, helium, through the tube and into the a GC/MS for analysis. Quantitation of identified species was approximated by using the external standard method and averaging the response factors for a range of alkanes and alkenes. Thus, the quantities reported should not be considered absolute, but can be used to compare relative amounts from test-to-test.

#### **RESULTS AND DISCUSSION**

When all of the data from the three engines are compared, a number of trends involving the effects of biodiesel on engine performance and exhaust emissions become apparent. Within these general trends, however, there are several instances where the data from one engine will diverge from the others. Average, transient composite regulated emissions for all three test engines, with and without catalyst, on all three test fuels are given in Table 3. Transient composite cycle work and fuel consumption data are also given in Table 3.

Test	Test		Transi	ent Em	issions,	g/hp-hr	BSFC,	Work,	Ref. Wor
Engine	Fuel	Catalyst	HC	CO	NOx	PM	lb/hp-hr	hp-hr	hp-hr
Cummins N14	B100	No	0.01	0.41	5.17	0.076	0.432	24.1	24.9
Cummins N14	B20	No	0.19	0.64	4.76	0.102	0.369	26.2	26.7
Cummins N14	2-D	No	0.23	0.75	4.57	0.106	0.383	26.7	27.3
DDC Series 50	B100	No	0.01	0.92	5.01	0.052	0.457	20.7	21.6
DDC Series 50	B100	Yes	0.02	0.76	4.90	0.030	0.446	20.8	21.5
DDC Series 50	B20	No	0.06	1.38	4.66	0.088	0.407	21.8	22.9
DDC Series 50	B20	Yes	0.04	1.24	4.63	0.059	0.404	21.8	22.9
DDC Series 50	2-D	No	0.06	1.49	4.50	0.102	0.400	22.2	23.2
DDC Series 50	2-D	Yes	0.03	1.43	4.51	0.075	0.397	22.1	23.1
Cummins B5.9	B100	No	0.08	1.27	4.90	0.081	0.521	11.3	11.5
Cummins B5.9	B100	Yes	0.06	0.95	4.91	0.040	0.524	11.3	11.6
Cummins B5.9	B20	No	0.21	1.61	4.79	0.109	0.467	11.9	12.1
Cummins B5.9	B20	Yes	0.15	1.21	4.88	0.069	0.475	12.0	12.2
Cummins B5.9	2-D	No	0.31	2.05	4.70	0.128	0.438	12.1	12.4
Cummins B5.9	2-D	Yes	0.19	1.52	4.75	0.077	0.452	12.1	12.3

TABLE 3. REGULATED TRANSIENT EMISSIONS

Engine-out, transient composite emissions of HC are shown in Figure 1 for all three engines on the three fuels. Using B100 generally resulted in a large reduction in measurable HC emissions, compared to 2D, for all three engines. In fact, HC emissions were nearly eliminated with B100 on all but the Cummins B5.9 engine. On B20, the drop in HC emissions was fairly consistent with the blend level. This was not the case for the Series 50 engine, but the Series 50 HC levels were so low that normal day-to-day variation in HC background levels likely caused variations in the data to be larger than the change in HC emissions expected with B20.

Engine-out CO emissions are given in Figure 2. Transient composite CO emissions were also significantly lower with B100 in all three engines, on average about 40 percent below the levels observed with 2D. This was likely due to the oxygen content of the B100 fuel. CO for all three engines generally responded in a linear fashion to oxygen content, yielding a smaller reduction in CO in proportion to the lower oxygen content of B20. For the B5.9 engine, a slightly larger than expected reduction in CO occurred with B20.

Transient composite  $NO_x$  emissions generally increased on B100 fuel, although the amount of change varied considerably depending on the engine. Engine-out  $NO_x$  emissions are given in Figure 3. The N14 and Series 50 engines were consistent, showing roughly a 12 percent  $NO_x$  increase on B100, and a four percent  $NO_x$  increase on B20. Figure 4 shows a plot of the change in  $NO_x$  emissions versus fuel oxygen content. Based on the data from these first two engines, the change in  $NO_x$  would

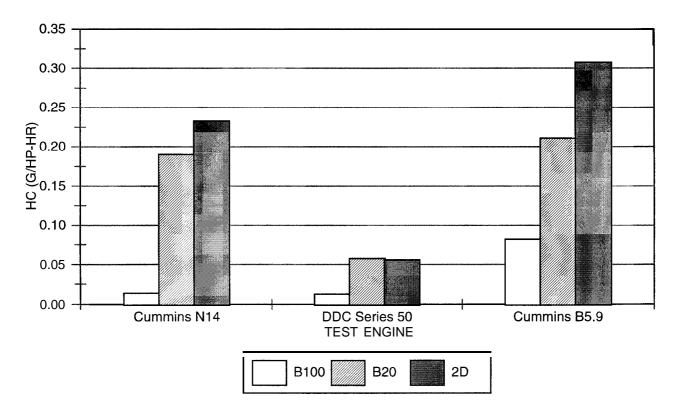


FIGURE 1. COMPOSITE TRANSIENT ENGINE-OUT HC EMISSIONS

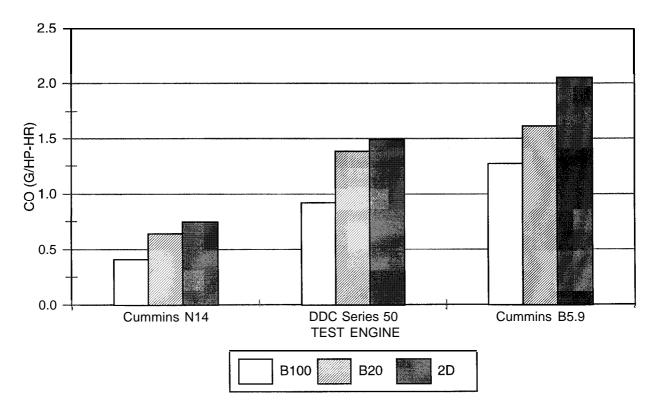


FIGURE 2. COMPOSITE TRANSIENT ENGINE-OUT CO EMISSIONS

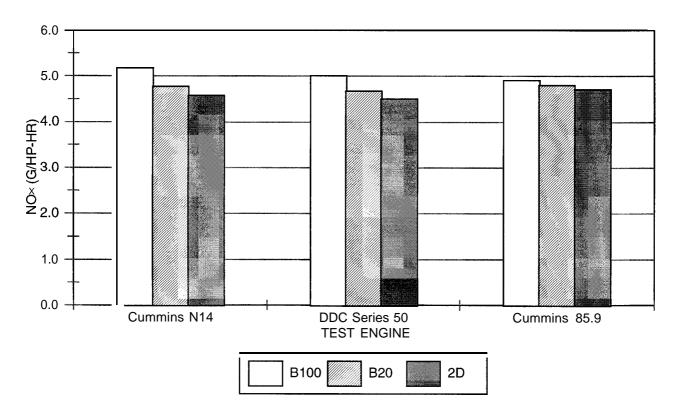


FIGURE 3. COMPOSITE TRANSIENT ENGINE OUT NO, EMISSIONS

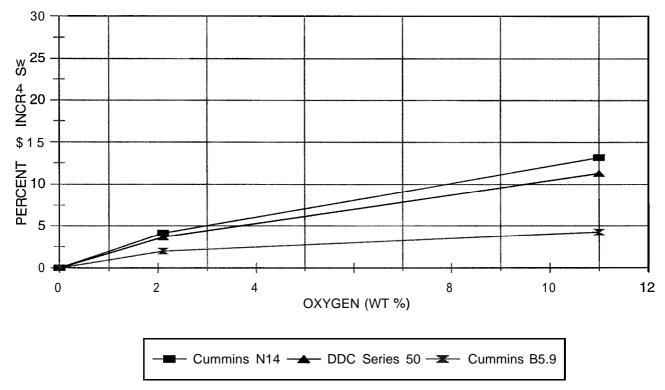


FIGURE 4. FUEL OXYGEN CONTENT VERSUS ENGINE-OUT NO,

appear to be tied in an almost linear fashion to the oxygen content of the fuel. However,  $NO_x$  emissions from the B5.9 engine showedvery little sensitivity to biodiesel and its corresponding oxygen content, with only a four percent increase in  $NO_x$  when B100 was used, and less than a two percent increase for B20.

Although all three engines were turbocharged, intercooled, and direct-injected, the B5.9 engine differs from the other two test engines in that the B5.9 employs a pumpline-nozzle fuel injection system with an inline fuel injection pump, while the other two engines employ electronic unit fuel injectors. The pump-line-nozzle method of fuel injection on the B5.9 operates at a significantly lower fuel injection pressure, as compared to the unit injector method. It is not known if the difference in NO, response to biodiesel between the B5.9 and the other two engines is a result of the difference in fuel injection method (and pressure), but it may indicate that another property besides oxygen content may also play a role in the general tendency to associate biodiesel with increased NO, emissions.

Engine-out particulate emissions for all three engines are shown in Figure 5, as well as the composition of particulate emissions. Total particulates were generally lower with increasing biodiesel content, again likely the result of the oxygen in biodiesel. However, considerable variation between engines is apparent.

Examination of the particulate composition data reveals a very consistent reduction in carbon soot with biodiesel. Figure 6 shows the percent change in soot versus fuel oxygen content. A disproportionate reduction is apparent, with less reduction achieved as the amount of biodiesel (and therefore oxygen) is increased. Biodiesel also reduced sulfates in a consistent manner, essentially because biodiesel does not contain any sulfur, and sulfates were essentially eliminated when using B100.

VOF emissions, presented as "oil" and "fuel+other" in Figure 5, tended to increase with increasing biodiesel content, although the amount of increase varied from engine-toengine. The lube oil portion of the VOF was unaffected by biodiesel, so the increased VOF was attributed to an increased fraction of unburned fuel, essentially the biodiesel fuel itself, which tends to condense on the filter media used to assess particulate emissions. The variation in increased VOF observed between the three engines accounts for the variation in the reductions observed in total particulates when biodiesel was used. The Series 50 engine had the smallest increase in VOF due to biodiesel, and therefore, it had the largest decrease in total particulate emissions. The N14 engine had the largest VOF increase, while the B5.9 engine fell between the other two engines.

The effect of biodiesel on engine performance was generally consistent for all three engines. Using B100 fuel resulted in roughly a seven percent loss of available torque at all engine speeds. This loss of torque is consistent with the lower volumetric energy content of the B100 fuel, as compared to 2D. This change is roughly equivalent to

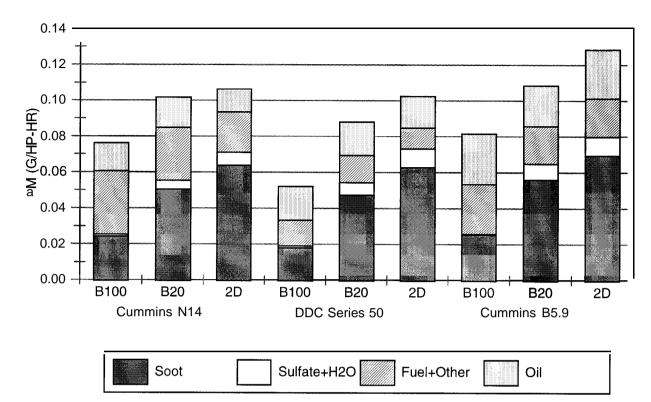


FIGURE 5. COMPOSITE TRANSIENT ENGINE-OUT PARTICULATE EMISSIONS

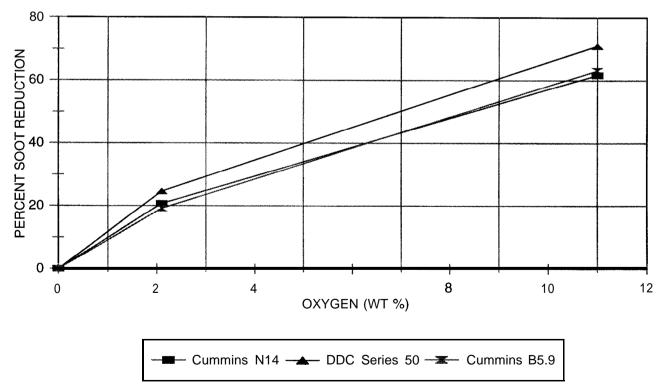


FIGURE 6. FUEL OXYGEN CONTENT VERSUS ENGINE-OUT SOOT

switching from 2D to 1D diesel fuel, assuming the engine is not recalibrated. The B20 blend was associated with a decrease of less than two percent in engine torque compared to 2D fuel, which was in proportion with the 20 percent biodiesel content of the blend.

Transient cycle fuel consumption was higher with B100, as compared to 2D fuel. With the N14 and Series 50 engines, transient cycle brake-specific fuel consumption (BSFC) was roughly 13 percent higher with B100, again due essentially the lower energy content of biodiesel. However, on the B5.9 engine, the BSFC was 17 percent worse with B100, a larger penalty than for the other two engines. This was also observed with the B20 blend, where the N14 and Series 50 engines showed essentially no change in BSFC with B20, while a six percent penalty was observed with the B5.9. The reason for the difference with the B5.9 is not known, but is may be related to fuel injection system differences, which also may have resulted contributed to the smaller NO, increase with the B5.9 engine as discussed earlier.

Figure 7 shows catalyst conversion efficiency for HC, CO, and particulate for all three fuels on the Series 50 and B5.9 engines. The N14 does not normally employ a catalyst, and was therefore not tested with one.  $NO_x$  was not affected by the catalysts. HC conversion efficiency data is not meaningful on the Series 50 engine because of the very low engine-out levels. With the B5.9 engine, HC conversion was slightly lower on both B100 and B20, although the catalyst-out HC levels were still below those observed with 2D. Transient composite CO conversion appeared to improve for the Series 50 engine with increased biodiesel content, while on the B5.9 engine, CO conversion was unaffected by biodiesel.

Catalyst conversion efficiency of total particulate was generally improved with increased biodiesel content. This is due to the tendency of biodiesel to shift particulate composition toward increased VOF content and decreased soot, and because the catalyst is primarily effective only on the VOF portion of total particulates. This shift in the character of the particulate can help to improve apparent catalyst conversion of the total particulate.

The  $C_1$  to  $C_{12}$  hydrocarbon speciation data indicated that a similar mix of compounds was present in the exhaust when using B100, B20, or 2D fuel, but that the mass of those compounds was significantly reduced on B100, and somewhat less on B20, compared to 2D. This was the case both with and without catalyst. Generally, no additional species of HC beyond those found for 2D was present in biodiesel exhaust. A summary of the engine-out  $C_1$  to  $C_{12}$  speciation data is given in Figure 8. B100 reduced the total mass of speciated hydrocarbons by about 50 percent on the N14 and B5.9 engines, and 30 percent on the Series 50. The effect of the blend varied from no change on the Series 50 to about a 30 percent reduction on the B5.9. Biodiesel and diesel exhaust hydrocarbons had about the same reactivity in terms of ozone formation potential. Generally the ozone potential was between five and six grams of ozone per

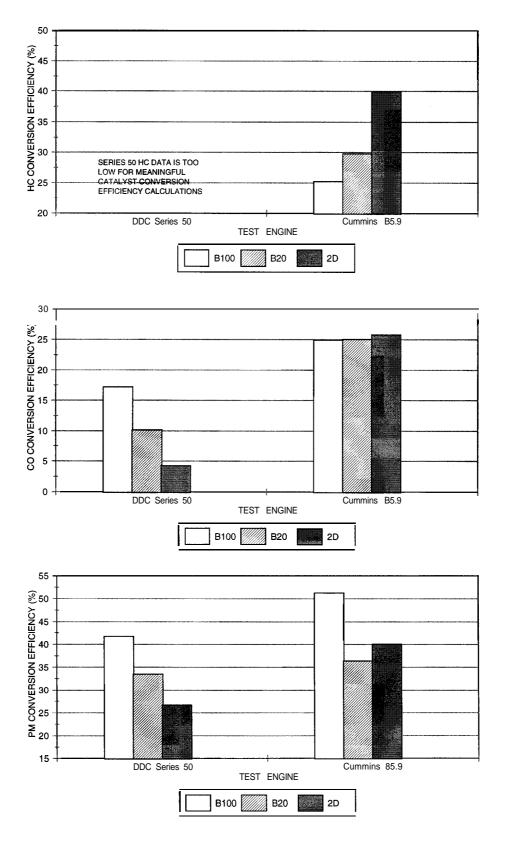


FIGURE 7. CATALYST CONVERSION EFFICIENCY

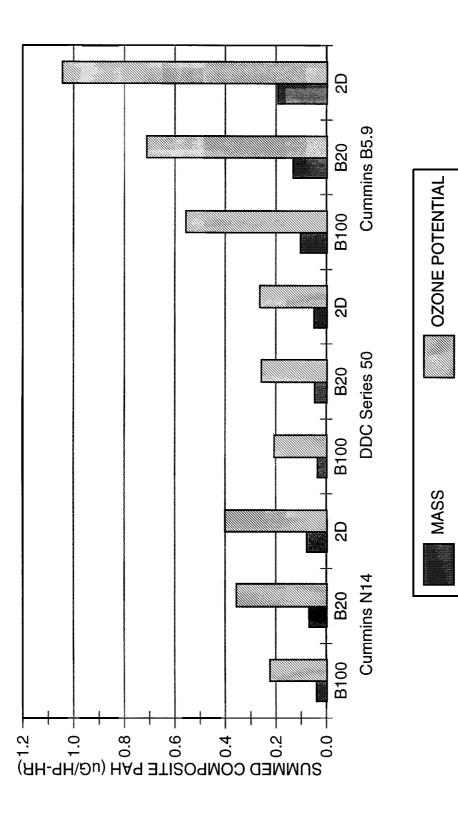


FIGURE 8. SUMMARY OF ENGINE-OUT C1 TO C12 SPECIATED MASS AND OZONE POTENTIAL FOR ALL ENGINES

gram of hydrocarbons.

The catalyst had no effect on speciated hydrocarbon mass for the Series 50, and only reduced about 20 percent of the speciated hydrocarbons for the B5.9, on any of the fuels. The catalyst tended to slightly increase the reactivity of the speciated hydrocarbons for all fuels on both engines.

PAH and nPAH data from all three engines indicated that the use of biodiesel generally resulted in decreased PAH and nPAH emissions. This is consistent with the fact that biodiesel itself does not contain any aromatics. Figures 9 and 10 show the transient composite total of PAH and the total of nPAH emissions, respectively, for all three engines and fuels. Using B100 substantially reduced engine-out PAH emissions from all three engines, with the largest decrease noted for the N14 engine, which also had the highest PAH emission levels on 2D fuel. The B20 fuel was associated with a smaller reduction in engine-out PAH levels, although the amount of reduction varied considerably from engine to engine. The catalysts also reduced PAH emissions on all three fuels, although the Series 50 catalyst appeared more effective than the B5.9 catalyst.

The emissions levels of nPAH compounds were significantly lower than PAH levels for all three engines. Using B100 nearly eliminated engine-out nPAH emissions on the N14 and Series 50 engines, and reduced them sharply on the B5.9 engine. B20 also lowered engine-out nPAH levels, but as with the PAH emissions, the amount of reduction varied from engine to engine. Using catalysts tended to increase nPAH emissions, regardless of fuel or engine. The reason for this increase is not known at this time.

A summary of the heavy-hydrocarbon GC/MS speciation data is given in Figure 11. In general, the higher molecular weight hydrocarbons were virtually eliminated with B100 fuel, except for small quantities of the methyl esters that made up the fuel. For B20, a mix of compounds were emitted, corresponding to exhaust species for both 2D and B100 exhaust, but with less total mass than for 2D fuel.

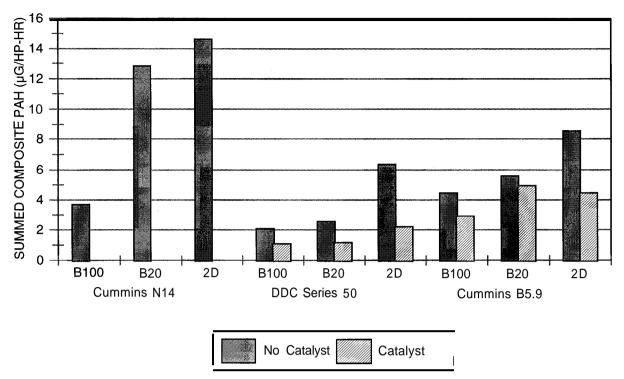


FIGURE 9. TOTAL ENGINE-OUT PAH EMISSIONS

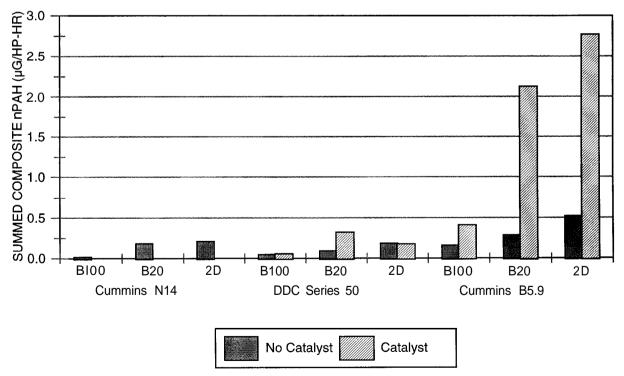
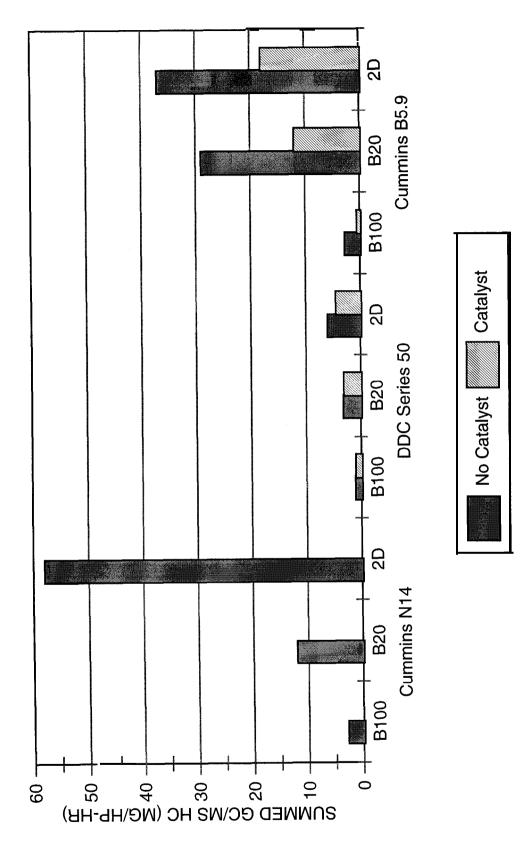


FIGURE 10. TOTAL ENGINE-OUT nPAH EMISSIONS





## CONCLUSIONS

Based on the data collected during this program, several general conclusions may be reached regarding the effect of biodiesel on diesel exhaust emissions.

Biodiesel was associated with lower emissions HC, CO, and particulates compared to levels associated with diesel fuel. These lower emission levels were likely due mostly to the fact that biodiesel contains about ten percent oxygen by weight, and this oxygen helps to oxidize these combustion products in the cylinder. With neat biodiesel, measurable HC emissions were generally eliminated, while CO was reduced roughly 40 percent from levels found on diesel. Particulate emissions were reduced between 25 and 50 percent, depending on the engine. In addition, the composition of engine-out particulate matter was shifted toward more volatile organic compounds and less carbon soot, creating a more favorable environment for treatment by a diesel oxidation catalyst.

Using biodiesel generally tended to increase NO, emissions. Substituting neat biodiesel for diesel fuel,  $NO_x$  emissions increased by roughly 12 percent, although the Cummins B5.9 engine demonstrated almost no change in  $NO_x$  emissions. The oxygen in biodiesel may be the cause of the observed  $NO_x$  increase, but this does not explain the lack of  $NO_x$  increase in the Cummins B5.9 engine. It is possible that other properties of biodiesel or interaction with characteristics of the combustion process and combustion chamber dynamics may cause variation in the expected trend toward higher  $NO_x$ . More research is needed to fully understand the dependence of  $NO_x$  emissions on biodiesel and other parameters.

Biodiesel was generally associated with a loss in engine power of about seven percent for the neat fuel, while with B20 power levels were within two percent of the levels observed on diesel fuel. Transient cycle fuel consumption was roughly 13 percent worse with the neat fuel, although the Cummins B5.9 engine demonstrated a larger penalty. With B20, transient cycle fuel consumption was essentially the same as with 2D, except for the Cummins B5.9 engine showed a six percent increase with B20.

Unregulated emissions data indicated that using biodiesel generally resulted in lower emissions of toxic and reactive hydrocarbons. Emissions of ozone forming compounds, including aldehydes, were substantially reduced with neat biodiesel. PAH and nPAH emissions were also substantially lower with neat biodiesel.

The 20 percent biodiesel blend directionally demonstrated many of the same trends observed with neat biodiesel fuel. However, the lower biodiesel content of the blend generally resulted in proportionately smaller changes in exhaust emissions, as compared to B100. In addition, the blend of biodiesel and diesel fuel did not generate any compounds in the exhaust which were not already present with one of the neat fuels.