

The Effect of Biodiesel Composition on Engine Emissions from a DDC Series 60 Diesel Engine

**Final Report
Report 2 in a series of 6**

M.S. Graboski, R.L. McCormick, T.L. Alleman,
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Colorado School of Mines
Golden, Colorado*



NREL

National Renewable Energy Laboratory

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Summary

The National Renewable Energy Laboratory (NREL) is conducting an investigation of various biodiesel fuels produced from waste oils. As a part of this study, data on emissions on the Environmental Protection Agency (EPA) heavy-duty transient cycle have been measured to demonstrate the sensitivity of engine emissions to biodiesel ester composition. The objective of the investigation was to determine the effect of biodiesel source material and ester molecular structure (number of double bonds and chain length) on particulate matter (PM), nitrogen oxides (NO_x), and certain unregulated pollutants. Testing included a series of fuels consisting of nearly pure fatty acid esters with different chain lengths and numbers of double bonds, as well as a number of fuels from practical feedstocks. A detailed analysis of the data was performed in an effort to determine how fuel chemistry and fuel properties correlate with the increase in NO_x emissions observed for many biodiesels here, and in most previous studies.

In total, 28 neat biodiesels and four B-20 blends (with EPA certification diesel) were tested. Seven fuels prepared from various natural feedstocks were obtained from the Institute of Gas Technology (IGT), and three of these were tested as B-20 blends. A methyl ester biodiesel prepared from soapstock was supplied by the Agricultural Research Service (ARS) and tested neat and as a B-20 blend. Twenty fuels were prepared at the Colorado School of Mines (CSM), primarily from nearly pure (or technical grade) fatty acids. Nevertheless, many of these fuels were not as pure as was originally intended because of high levels of impurities in the feedstocks. These fuels covered a very wide range of realistic feedstocks as well as systematically varying chemical properties such as fatty acid chain length and number of double bonds in the fatty acid chain. Fuels were analyzed for a wide range of properties including water and sediment, free and total glycerine, iodine number, peroxide value, acid number, cetane number, density, kinematic viscosity, gross heating value, and carbon, hydrogen, and oxygen content. The specific fatty acid esters present in the fuels were also determined by GC/MS analysis. Regulated pollutant emissions, along with certain non-regulated pollutants, were measured on a 1991 DDC Series 60 engine via the heavy-duty transient test (40 CFR Part 86 Subpart N). Emissions from biodiesel fuels were bracketed with emissions for EPA certification diesel. This allows comparison with a conventional diesel, and most importantly, a measure of engine drift. Volatile organic fraction, PM sulfate, and emissions of certain aldehydes were measured for many of the fuels. Samples for biological activity analysis by the University of California at Davis were collected.

All fuels prepared at CSM met water and sediment specifications as well as free and total glycerine specifications (with the exception of one fuel produced with high glycerine value on purpose). Not all fuels met the acid number specification, in particular fuels with a high stearate content as these were not liquid at or near room temperature making acid removal difficult. Fuels prepared by IGT met the water and sediment specifications immediately after synthesis based on analyses supplied by IGT. However, problems associated with water were evident when these fuels were received at CSM, indicating that the hygroscopic character of these esters can create problems during storage and transport. Other properties are generally in good agreement with literature values.

Certification fuel runs exhibited a mean NO_x emission level of 4.59 g/bhp-h (+/-0.053) with no significant drift over the four month test program. PM emissions averaged 0.261 g/bhp-h (+/-0.019). A small downward drift in PM emissions was evident (11% over the course of the project). Thus, no correction for drift was applied to the NO_x emissions data but a small correction was applied to PM.

Testing the biodiesels produced from natural sources (supplied by IGT and ARS) indicated that PM emissions did not depend on molecular structure but were dependent on the oxygen content of the fuel only. All fuels reduced PM relative to certification diesel. NO_x emissions varied considerably with biodiesel feedstock but all increased NO_x relative to certification diesel. The most highly unsaturated fuels (canola, soy, and soapstock) produced the highest NO_x emissions. Soy and soapstock biodiesels produced very similar emissions, as expected. Btu based fuel economy was the same for all biodiesels and certification fuel.

For the fuels prepared from nearly pure esters, all reduced PM relative to certification diesel but the PM reduction was not proportional to oxygen content in all cases. Almost all of these fuels increased NO_x relative to certification fuel. The exceptions were the highly saturated esters methyl palmitate, methyl laurate, ethyl and methyl stearate, and ethyl ester of hydrogenated soybean oil. No consistent difference in emissions was observed between ethyl and methyl esters of the same feedstock. High peroxide value (1800), acid number, and glycerine content had no effect on regulated pollutant emissions in this short-term study. These out-of-spec fuel properties may cause fouling or storage and handling problems in longer-term studies.

The VOF emission for certification fuel (5.5% of 0.261 g/bhp-h PM) is 0.0144 g/bhp-h. For the biodiesels on average (21.4% of 0.07 g/bhp-h), it is 0.0150 g/bhp-h (results for biodiesels from real-world feedstocks). Neat biodiesel contains no sulfur and so sulfate emissions are significantly less for these fuels. Aldehyde emissions from the various biodiesels are not significantly different from aldehyde emissions from certification diesel fuel.

Regression analysis of the results indicated that emissions could be correlated by one parameter. PM reduction was proportional to oxygen content for biodiesels with a cetane number of greater than about 45 (density greater than 0.89). For fuels with cetane number less than 45, PM reduction was less. NO_x emissions were also well correlated with a single parameter, either density or cetane number (which were highly correlated with each other). The results suggest that neat biodiesels with cetane numbers greater than about 68 may produce NO_x emissions equal to or less than certification fuel. The impact of molecular structure is implicit in either the density or cetane number. More saturated esters have higher cetane numbers and lower densities than less saturated esters. Thus, the lower the iodine number, the lower the NO_x emissions. These conclusions apply to natural cetane number, the impact of cetane enhancing additives may be different. Data collected also demonstrate the effect of chain length. The density of shorter chain length saturated esters is greater than longer chain saturated esters and the NO_x emission is greater. Note that methyl laurate (12 carbon fatty acid chain), with cetane number 61.2 and density 0.873, is NO_x neutral compared to certification fuel. The important conclusion is that fuel chemistry is at the root the fuel properties that effect emissions, and in particular the increased NO_x emissions observed for many biodiesel fuels.

It is important to note that the results presented here are engine specific. Other engines and calibrations will probably give similar results. The impact of the NO_x/PM tradeoff for specific diesel engines will change the overall results but probably not the trends.

The NO_x behavior of biodiesel blends is complex. Insufficient physical property data are available to characterize the effect of blending at this time, although provisionally for 25 blends a linear combination of NO_x emissions seems appropriate. The effect of oxygen on particulate matter is well characterized by considering only the oxygen content of the blend. This conclusion appears to be robust.

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Introduction

The National Renewable Energy Laboratory (NREL) is conducting an investigation of various biodiesel fuels produced from waste oils. As an important part of this study, data on emissions measured with the EPA heavy-duty transient cycle are necessary to demonstrate the possible sensitivity of engine emissions to biodiesel ester composition. We report regulated emissions for hot and cold start tests for biodiesel produced from various feedstocks, as well as results for certain non-regulated pollutants. Additionally, to understand the impact of biodiesel composition on emissions, we have prepared a series of fuels consisting of nearly pure fatty acid esters. This test matrix allows an evaluation of the effect of chain length and number of double bonds, as well as other properties, on nitrogen oxides (NO_x) and particulate (PM) emissions and fuel properties.

Background

Oxygenated fuels have a history of reducing exhaust emissions from motor vehicles. Additions of methyl-tertiary-butyl ether (MTBE) and ethanol have shown success in reducing emissions from gasoline engines. In high polluting automobiles, oxygenated gasoline can decrease carbon monoxide (CO) up to 50%. Oxygenates are now mandated under the Clean Air Act for use in reformulated and CO control gasoline. The success of oxygenated gasoline has sparked interest in the use of oxygenated compounds as emissions reducing additives in diesel fuel. Oxygenated compounds used as diesel additives are structurally similar to diesel fuel but have one or more oxygen atoms bonded to the hydrocarbon chain. Numerous oxygenated compounds have been investigated as either diesel fuel additives or replacements and have shown emissions reducing properties. Oxygenated fuels are also of special interest since they are a potential renewable source of energy.

Liotta and Montalvo (1993) investigated the emissions effects of several different oxygenated compounds used as diesel fuel additives. Oxygenates were selected on the basis of economic viability as an additive, toxicity, and fuel blending properties. Important fuel blending properties included: solubility, flash point, viscosity, water solubility, and water partitioning of the oxygenate. Three glycol ethers, an aromatic alcohol, an aliphatic alcohol, and polyether polyol were selected for evaluation. The actual structures of these compounds were not revealed. Methyl soyester and diglyme were also included for comparison to previous results. Most of these oxygenates were cetane neutral (cetane number similar to diesel) so that the fuel cetane number was considered to be constant. Based on heavy-duty transient testing, PM and CO were generally reduced, and *NO_x showed an increase with all oxygenates studied*. The PM reduction experienced appeared to be related to the amount of oxygen in the fuel. Unregulated emissions of aldehydes and ketones were reported to decrease upon addition of oxygenates to the fuel.

Nikanjam (1993) looked at the possibility of producing an additive treated diesel fuel that generates emissions equivalent to a CARB 10% aromatic reference fuel. Oxygenated compounds were considered as an option to reduce emissions. Ethylene glycol monobutyl ether acetate was selected for testing based on cost, fuel blending properties, and toxicity concerns. Emissions results showed CO and PM reductions of approximately 18% and *a NO_x increase of 3%*. Since NO_x reduction was the most difficult obstacle in showing equivalence between the test fuel and the 10% aromatic reference fuel, no further testing was done on oxygenates.

Ullman and coworkers (1994) and Spreen and coworkers (1995) examined the effect of diesel fuel properties, including oxygenates, on emissions from engines having both 5 g/bhp-h (1994) and 4 g/bhp-h (1998) calibrations. Ullman and coworkers studied diglyme at up to 4 wt% in a DDC Series 60 engine. They observed that for the 5 g/bhp-h calibration *addition of oxygenate caused an increase in NO_x*.

Particulate was reduced substantially. For the 4 g/bhp-h calibration no increase in NO_x was observed. Spreen and coworkers examined the addition of diglyme and monoglyme (ethylene glycol dimethyl ether) in a Navistar DTA-466 equipped with an oxidation catalyst. They observed similar results for diglyme, however *with the lower boiling monoglyme no increase in NO_x was noted*, even for the 5 g/bhp-h calibration. In all cases particulate reduction was related only to the oxygen content of the oxygenated additive.

Ortech International (1993) has found that NO_x emissions in Detroit Diesel 2-stroke engines increase with the addition of methyl soyester while particulate emissions decrease. Using a 1991 6V-92TA DDEC II engine, NO_x emissions were found to increase by 3.5%, 5.5%, 13.4%, and 15% respectively for 10%, 20%, 30%, and 40% blends. Timing changes can be used to reduce NO_x emissions but particulate reductions are smaller. Graboski and coworkers tested methyl soyester and diesel-soy ester blends in a 1991 Detroit Diesel Series 60 (4-stroke) engine. For 35% biodiesel, the composite NO_x emission increased by nearly 1%, while the composite particulate emission decreased by 26% relative to the reference diesel. The NO_x increase of 1% was found to be statistically significant at the 99% level. For 100% biodiesel, the composite NO_x increased by 11% while PM was decreased by 66%. McCormick and coworkers (1997) investigated 1% oxygen in diesel using a 6V-92TA DDEC II engine. Oxygen was added as a C₈ (n-octanol), C₁₂ (decanoic acid), and C₁₇ (methyl soyester). Relative to the base diesel, the NO_x changes were -1.12%, 0.36%, and 2.29%. The NO_x increase for methyl soyester is in good agreement with the Ortech work. This study also examined the effect of n-octanol and methyl soyester at 2% oxygen on NO_x emissions from a 1991 DDC Series 60 engine. Octanol reduced NO_x by 2.9% while methyl soyester increased NO_x by 2.53%. Thus, data from two studies suggests that lower molecular weight or lower boiling point oxygenates might not affect NO_x as greatly as methyl soyester. A number of other studies have also shown increases in emissions of NO_x for biodiesel fuels, notably recent studies reported by Sharp (1998) and by Smith and coworkers (1998). However there are also several significant studies where an increase in NO_x is not observed. For a more detailed discussion see the review paper by Graboski and McCormick (1998).

A number of fuel properties have been shown to effect emissions of NO_x. Fuel density is known to effect emissions of NO_x from diesel engines. For example, Signer and coworkers (1996) report a 3% to 4% increase in NO_x for a 3.5% increase in fuel density using the EEC 13-mode test cycle. Cetane number and fuel aromatic content are well known to influence NO_x and PM emissions from diesel engines (Ullman, et al., 1990). For biodiesel blends with diesel, the blend aromatic content is lower than that of the base diesel fuel (biodiesel contains no aromatics). This dilution of the aromatics should lower both PM and NO_x emissions. Biodiesels also have increased cetane number relative to typical No. 2 diesel, which should reduce both emissions.

Objectives

The studies cited above clearly indicate that substantial reduction in particulate emissions can be obtained through the addition of oxygenates, and in particular biodiesel, to diesel fuel. There is also strong evidence that soy derived biodiesel can cause NO_x emissions to increase. However, some studies find no NO_x increase. Comparison between studies is confounded because of the use of different engines and biodiesel from different sources. *The objective of the current investigation is to determine the effect of biodiesel source material and ester molecular structure (number of double bonds and chain length) on PM, NO_x, and certain unregulated pollutants.* We have carefully quantified emissions from different biodiesel fuels, from a variety of real-world source materials as well as fuels produced from pure fatty acids, on one engine. A detailed analysis of the data is presented in an effort to determine what fuel properties are correlated with the increase in NO_x emissions observed in most studies.

Methods

Fuels and Test Matrix

The reference fuel for this test program was certification diesel fuel obtained from Phillips Petroleum (Lot D434). The properties of this fuel are shown in Table 1. The reference diesel was used in preparing B-20 blends. Additionally, tests on the reference diesel were performed both before and after each biodiesel fuel to provide an indication of engine drift. The test sequence actually used is shown in Appendix A. Two sets of biodiesel fuels were tested. A set of seven neat biodiesels from various feedstocks was supplied by IGT. A biodiesel prepared from soapstock was supplied by ARS (Haas and Scott, 2000). All neat fuels were tested and four were tested as B-20 blends. The second set of fuels was prepared by CIPHER from pure, or nearly pure, fatty acids and from several feedstock fats (except methyl soyester which was obtained from a commercial supplier). The fuels examined in this study are listed in Table 2.

Table 1. Properties of certification diesel fuel Lot D-434 used as reference in this study.

Property	<i>Lot D-434</i>	<i>ASTM Method</i>
API Gravity	36.28	D-287
Viscosity, cs 40°C	2.5	D-445
Net BTU/lb	18456	D-3338
Cetane Number	46.0	D-613
Carbon, wt%	86.6	D-5291
Hydrogen, wt%	13.4	D-5291
Oxygen, wt%	0	D-5291
Sulfur, ppm	300	D-2622
Nitrogen, ppm	--	D-4629
IBP, F	353.9	D-86
T50, F	498.7	D-86
T90, F	583.7	D-86
EP, F	646.4	D-86
Aromatics, vol%	29.2	D-1319
Olefins, vol%	2.0	D-1319
Saturates, vol%	68.8	D-1319

Our original contract with NREL called for making (or acquiring) and testing 18 fuels. As Table 2 shows, 20 fuels were prepared by CSM. There was some deviation from the original plan. The methyl soyester employed was a commercially available biodiesel known as “Soyagold.” This methyl ester was transesterified with ethanol to prepare the ethyl soyester. Only a small quantity of linolenic acid was available from the supplier, and this was used to prepare most of the methyl linolenate. To satisfy the need for tri-unsaturates, linseed oil was used as an additional unsaturated fatty acid, to supply some fraction of the methyl linolenate. We originally planned to prepare ethyl linolenate, however this fuel was made entirely from linseed oil, as was the methyl linseed ester originally specified for blends of stearate and linolenate esters. We also originally planned to produce highly oxidized samples of methyl and ethyl linolenate by oxidation in the laboratory. However, we had 50 gallons of highly oxidized (peroxide value of about 2000) methyl soy ester stored in our lab, and utilized this material instead. This material had become oxidized over several years of storage at room temperature. Oxidized ethyl esters were prepared by transesterification of this material with ethanol.

Table 2. List of biodiesel fuels tested in this study, actual test sequence in Appendix A (LFFAG=low free fatty acid grease, HFFAG=high free fatty acid grease).

Fuels Tested

Supplied by IGT

Methyl Soy
 Edible Methyl Tallow
 Inedible Methyl Tallow
 Methyl Canola
 Methyl Lard
 Methyl LFFAG
 Methyl HFFAG
 B20 Inedible Methyl Tallow
 B20 Methyl Soy
 B20 Methyl LFFAG

Supplied by ARS

Methyl Soapstock Ester
 B-20 Methyl Soapstock Ester

Prepared at CSM

Methyl Laurate
 Methyl Palmitate
 Methyl Stearate
 Ethyl Stearate
 Methyl Oleate
 Ethyl Oleate
 Methyl Linoleate
 Ethyl Linoleate
 Methyl Linolenate
 Ethyl Linseed
 Methyl Soy (Soyagold)
 Methyl Hydrogenated Soy
 Ethyl Soy
 Ethyl Hydrogenated Soy
 2:1 Methyl Stearate:Methyl Linseed
 1:2 Methyl Stearate:Methyl Linseed
 Oxidized Methyl Soy
 Oxidized Ethyl Soy
 High Acid Number Methyl Oleate
 High Glyceride Ethyl Soy

Fuel Specification:

In most cases the fuels tested met the NBB specification for biodiesel shown in Table 3. In a number of circumstances, it was not possible to meet the specification, as it was developed for soy diesel. This is discussed in the emissions testing section.

Table 3. NBB Specification for pure (100%) biodiesel.

Property	ASTM Method	Limits	Units
Flash Point	93	100 min	°C
Water and Sediment	2709	0.05 max	Vol %
Carbon Residue	4530	0.05 max	Wt %
Sulfated Ash	874	0.02 max	Wt %
Kinematic Viscosity@40°C	445	1.9-6.0	mm ² /sec
Sulfur	2622	0.05 max	Wt %
Cetane Number	613	40 min	
Cloud Point	2500	Report	°C
Copper Strip Corrosion	130	No. 3 max	
Acid number	664	0.80 max	Mg KOH/gm
Free Glycerine	GC ¹	0.02 max	Wt %
Total Glycerine	GC ¹	0.24 max	Wt %

¹Christina Planc procedure

Fuel Preparation:

Apparatus: Two identical reactors were built. Each reactor consisted of a 22 L round bottom heavy walled three neck flask surrounded by and supported in a heating mantle which was located in a floor cradle. The central larger bore, 55/50, neck contained a water cooled stirrer bearing. This supported a 4-foot heavy-duty stirrer shaft that was driven by a high torque, 0-1000 rpm laboratory stirrer and propelled a Teflon stirrer blade. One of the smaller bore, 24/40 side arms of the flask was connected to a custom distilling head, above which were two condensers in series. The reactants were degassed by purging with argon for several minutes. During reaction, argon was introduced to the system through the top of the condenser. The distilling head allowed the collection of a 500 cm³ volume of distillate or, via a three way tap, the distillate could be returned directly to the reactor or diverted to a 5 gallon plastic drum for collection. The other smaller bore, 24/40, side arm of the reactor was used for the introduction and removal of reagents via either a funnel or a pressure equalizing calibrated addition funnel and was stoppered when not in use. The whole system was greased with Krytox[®] grease, a non-contaminating, non-flammable, fluorinated grease manufactured by Dupont. The temperature of the reaction was measured on the outside skin of the reactor by a thermocouple both above and below the reaction volume. A control box was custom made to control power to the heating mantles, stirrer motors, and the supply of water. The reactor assemblies were mounted with Unistrut on a steel base plate, which had a waterproof lip to provide secondary containment. The whole assembly stood within a plastic sheathed temporary laboratory housing, which provided tertiary containment. A list of purchased parts is provided in Appendix B.

Synthesis: Methyl soy ester was obtained from a commercial supplier. Oxidized methyl soy ester was a commercial biodiesel that had “aged” in our laboratory for several years. Ethyl esters of these two fuels were prepared by transesterification with ethanol. Other fuels were prepared from fatty acid or fat feedstocks. In general all manipulations were carried out under argon. An example of each class of

synthetic reaction is given in Appendix B. All fuels were stored under argon in cans containing muslin bags of the desiccant sodium sulfate. The methanol used in these reactions was recycled after drying.

Fuel Property Measurement:

Methods used for fuel property measurement are listed in Table 4. Neat biodiesels obtained from IGT were analyzed for cetane number, gross heating value, and carbon, hydrogen and oxygen. B-20 blends were analyzed for carbon, hydrogen, and oxygen. Available analytical data for the soapstock methyl ester were supplied by ARS. Biodiesel fuels produced at CSM were analyzed for a number of other properties, listed below. Cetane numbers were not measured for fuels that were solid at room temperature because Core Laboratories had no method for handling such fuels.

Table 4. Analytical methods used to determine fuel properties.

<i>Property Measured</i>	<i>Method</i>	<i>Laboratory</i>
Water and Sediment	ASTM D-2709	Williams
Free and Total Glycerine	Christina Planc	Williams
Iodine Number	ASTM D-1510	CSM
Peroxide Value	ASTM D-2340	Williams
Acid Number	ASTM D664	CSM
Cetane Number	ASTM D-613	Core
Density	ASTM D-4052	Core
Kinematic Viscosity	ASTM D-445	Core
Gross Heating Value	ASTM D-240	Core
Carbon, Hydrogen, Oxygen	ASTM D-5291, oxygen by analysis	Core

Ester Speciation:

Fatty acid speciation was performed in-house using a GC-MS method employing a HP 5890 GC equipped with a 5970 Mass Selective Detector. The column was a 0.2mm I.D. 12 m HP cross-linked methyl silicone high performance capillary column. The column is run in splitless mode using the following temperature program:

- 5 minutes at 70 °C, to elute solvent
- 5 °C minute⁻¹ to 205 °C
- 5 minutes at 205 °C, to separate the C18 esters
- 5 °C minute⁻¹ to 280 °C
- 3 minutes at 280 °C, to elute any heavier material than C22 esters.

Method development and calibration are performed using a fatty acid methyl ester (FAME) mix in methylene chloride. This standard mixture of known concentrations is representative of grain fats and was supplied by Supelco. The mix contains FAME's from C8 to C22, from fully saturated to tri-unsaturated. For each biodiesel sample, a 1 cm³ aliquot is mixed with 3 cm³ of HPLC grade hexane. Two injections are then performed. A 0.5 uL injection is used to speciate the impurities, and a 0.2 uL injection is used to analyze for the major components.

Emissions Testing

The system for emissions measurement for regulated pollutants (THC, CO, NO_x, and PM) includes supply of conditioned intake and dilution air, an exhaust dilution system, and capability for sampling of particulate and analysis of gaseous emissions. All components of the emissions measurement

system meet the requirements for heavy-duty engine emissions certification testing as specified in Code of Federal Regulations Title 40, Part 86, Subpart N.

Test Engine:

The engine is a 1991 calibration, production model loaned by the Detroit Diesel Corporation. The six cylinder, four stroke engine is nominally rated at 345 bhp (257 kW) at 1800 rpm and is electronically controlled (DDEC-II), direct injected, turbocharged, and intercooled. Engine specifications are listed in Table 5.

Table 5. DDC Series 60 engine specifications and mapping parameters.

Parameter	
Serial Number	6R-544
Displacement	11.1 L
Rated Speed/Horsepower	1800 rpm/345 bhp
Max Torque Speed/Max Torque	1200 rpm/1335 ft-lb
Idle Speed/Citt	600 rpm/0 ft-lb
High Idle Speed	1940 rpm
Intake Depression	-16 ± 1 in H ₂ O
Backpressure	32.6 ± 3 in H ₂ O
Aftercooler Dp	40 ± 3 in H ₂ O
Intake Manifold Temperature	44±2°C

Quality Control:

The testing is carried out in accordance with 40 CFR Part 86 Subpart N. In addition, a number of additional measures are taken to insure that the NO_x and PM emissions collected in this program are both precise and accurate.

Emission Gas Standards: Emission gases are 1% EPA Protocol Standards. Gas standards were not changed during this test program.

Carbon Balance: As a test quality-assurance check, a carbon balance is performed for each transient test. Diesel mass fuel consumption was monitored with a Micromotion DP-25 mass flow sensor and by weighing the fuel supply tank before and after a test using a load cell. Exhaust carbon is determined from the background corrected THC, CO, CO₂, and PM emissions data. The fuel analysis is used to estimate the H/C ratio of the THC. PM is assumed to be 100% carbon. Runs where carbon balance closure was more than +/-6% in error were generally rejected.

NO_x Humidity Correction: Humidity has a large influence on NO_x emissions. Humidity is measured continuously in the conditioned air inlet by two independently calibrated methods: a dew point meter and a polymer membrane sensor. Furthermore, the intake air is controlled to a 53°F (11.7°C) nominal dew point to insure that the NO_x correction factor (40 CFR 1342-94(d)(8)(iii)) is very near one and essentially constant from test to test. The two humidity measurements do not produce NO_x correction factors that differ by more than 2%.

The Effect of Intake Manifold Temperature on NO_x Emissions: The engine is equipped with a water cooled turbocharger intercooler. The supply temperature and flow rate of cooling water to the intercooler are adjusted during the engine mapping process to match the manufacturer's design temperature for the intake air at rated speed and wide open throttle. The flow and inlet temperature are

feedback controlled so that the temperature history of the manifold from test to test is repeatable. The manifold air temperature changes with load and speed but the objective is to always keep the same profile from test to test. The maximum temperature and stage where it occurred are logged during each test to confirm that NO_x differences are not related to variations from test to test in the intake air temperature profile.

Regulated Gaseous Emissions Measurement:

All gas mass emissions are determined by background corrected flow compensated integration of the instantaneous mass rates. Tedlar bag samples of background and sample are also collected. The exhaust sample is proportionally sampled through a critical flow orifice. The bag compositions are compared with the bag equivalent flow compensated emissions to validate the test runs. Agreement is always within 5% for the individual regulated gaseous emissions.

Particle Sampling for Mass:

Particulate matter is collected on Pallflex T60A20 70 mm filters of a common lot. Particulate matter is sampled through a secondary tunnel which insures a filtered gas temperature below 52°C (126°F). Two independent mass flow controllers are used to regulate the total filtered gas sample and the secondary dilution air rate. The computer determines the total sample volume by integrating the instantaneous flow difference. Flow is made proportional to the diluted exhaust by sending a varying secondary air flow set point from the test manager computer which is based upon the CFV flow rate which in turn is a function of the diluted exhaust temperature at the venturi. The apparent sample flow rate depends on zero flow analog voltage outputs from the transmitters. These are logged before and after the test and the corrected integrated volume is established with a calibration model that considers the voltage offsets.

PM Background: Parallel background samples were not collected. Instead, the intake air is filtered to 95% ASHRAE efficiency and periodic background checks are made. Demineralized water is used for humidity control. The mass collected in the background check made during this program were extremely small. No background correction was made to the particulate determinations.

Weigh Room Conditions: Since the PM mass collected especially for the biodiesel samples was small, even minor differences in filter weight due to water adsorption can impact the particulate mass emission. Particle filter handling and weighing is conducted in a yellow light, constant humidity weigh room held at 9±2°C (48±4°F) dew point, 50% nominal relative humidity, and 22±1°C (72±2°F).

Special Analytical Procedures:

Volatile Organic Fraction (VOF) and Sulfate: VOF was determined using a procedure developed by Navistar. A vacuum oven is maintained at 225°C, a vacuum level greater than 20 in Hg, and with a very low flow of purge air. Particulate filters equilibrated in the constant temperature, constant humidity weigh room are weighed and then rapidly inserted into the oven. Vacuum and purge airflow is initiated and filters are maintained in the oven for 2.5 to 3.0 hours. The oven is then pressurized and the filters quickly removed. After re-equilibration in the weigh room, the filters are weighed and VOF is determined as the difference between the initial and final weights.

Sulfate analysis was contracted to an outside lab (Hazen Research, Inc. of Golden, Colorado) and was performed following the procedure outlined by the Coordinating Research Council (1987). The procedure involves washing the filters with a carbonate/ bicarbonate solution to dissolve the sulfate. Any

filter material is then removed and the solution is injected into an ion chromatograph. The sulfate is determined by comparison against a four-point calibration curve using potassium sulfate as a standard. Thus, this procedure measures the sulfate fraction of total primary PM and does not include other forms of sulfur that are not water soluble. Sulfate analysis was performed only for the biodiesels prepared from various waste and agricultural sources and supplied by IGT.

Aldehyde Sampling and Analysis: To collect samples for aldehyde analysis a system which collects proportional, diluted exhaust samples in accordance with the Code of Federal Regulations (CFR 40 Part 86 Subpart N) is employed. The sampler is regulated by a mass flow controller driven by set points issued in response to the exhaust tunnel temperature. The test computer logs this flow rate. The sampling system is fitted with DNPH sorbents for aldehyde sampling (Model S-10, Catalog No. 21014 obtained from Supelco). The sorbents and analysis methods follow EPA Method TO-11. Crotonaldehyde is used as an internal standard. Analysis was performed by Peak Analytical of Pearland, Texas. The DNPH sorbents are extracted and then analyzed by HPLC with UV detection for aldehydes including:

- Formaldehyde
- Acetaldehyde
- Propionaldehyde
- Hexanal
- Heptanal
- Octanal or Caprylaldehyde
- Nonal
- Decanal or Capraldehyde

Aldehyde emissions were measured only for the biodiesels prepared from various waste and agricultural sources and supplied by IGT.

PM Sampling for Studies of Biological Activity Analysis: Samples were collected for study by Dr. Norman Kado of the University of California at Davis. Particulate matter filters, identical to those used for mass PM determination as described above, were sent to Dr. Kado for precleaning. These precleaned filters were then used to sample PM using a sampling system identical to that described for aldehyde sampling. The samples were weighed, placed in glassine envelopes, labeled, wrapped in foil, sealed in polyethylene bags, and stored at -20°C. Samples were shipped overnight in insulated containers with blue ice. These samples were collected for the biodiesels prepared from various waste and agricultural sources and supplied by IGT.

Results Part I: Fuel Properties

The fuel properties measured included both those applicable to the National Biodiesel Board (NBB) standard and other properties to characterize the fuels in more detail and correlate their emissions. Table 3 presented the biodiesel fuel specification. Because many of the fuels were manufactured from non-traditional feedstocks, their properties could be outside allowed ranges in the proposed specification. From a fuel performance perspective the key NBB specification properties are water and sediment, cloud point, sulfated ash, sulfur, acid number, free glycerine, and total glycerine. In terms of emissions, cetane number, density, carbon residue, viscosity, iodine number, heating value, oxygen content, and fatty acid profile are relevant.

Biodiesels from Non-traditional Feedstocks

In this program, IGT provided six feedstocks made from non-soy fats plus a soydiesel. IGT also provided some analytical data for these materials. One biodiesel was also supplied by ARS along with analytical results. The relevant data for emissions modeling is included in the summary table discussed later in this chapter. In addition, CSM also contracted Core Laboratories to perform certain property measurements for these fuels.

Core Laboratories analyzed the B20 blends for carbon, oxygen, and hydrogen content and the seven neat biodiesels for carbon, oxygen, hydrogen, cetane number, and gross heating value. These results are summarized in Table 6 and analysis reports are in Appendix C. Carbon, oxygen, and hydrogen values for the B-20 fuels are from actual fuel analyses. There is a general inconsistency between the cetane numbers measured by Core Laboratories and those provided by IGT. Additional fuel analysis data were reported to NREL by IGT for most of these fuels. These data are included as Appendix D. Data supplied by ARS for the soapstock methyl ester are reported in Appendix E.

Table 6. Analytical results for neat biodiesels and B-20 blends.

Sample	Carbon wt%	Oxygen wt%	Hydrogen wt%	Cetane Number	Heat of Combustion, btu/lb	
					Gross	Net
Methyl Soy, Neat	76.25	11.16	12.59	47.2/59*	17130	15940
Edible Methyl Tallow, Neat	75.15	11.74	13.11	62.9/64.8*	17120	15881
Inedible Methyl Tallow, Neat	75.30	11.08	13.62	61.7/54.3*	17128	15841
Methyl Canola, Neat	76.12	11.04	12.84	55.0/53.9*	17074	15861
Methyl Lard, Neat	75.03	11.82	13.15	63.6/NA*	17084	15841
Methyl LFFAG, Neat	75.71	11.10	13.19	57.8/52.2*	17133	15887
Methyl HFFAG, Neat	76.06	11.28	12.89	52.9/53.2*	16928	15710
B20 Inedible Methyl Tallow	83.43	2.73	13.84	49.1**		17933**
B20 Methyl Soy	83.51	2.52	13.97	46.2**		17953**
B20 Methyl LFFAG	83.65	2.31	14.04	48.4**		17942**

* Reported by IGT

** Calculated assuming linear blending by volume or weight fraction.

Biodiesels from Pure or Nearly Pure Esters

Table 7 shows properties measured for fuels prepared under this project. AG Environmental Products donated the methyl soy ester. It has been proposed that glycerine will impact emissions both immediately due to its different chemical structure and long term due to injector fouling. All fuels prepared by CSM easily meet the specification for free glycerine (0.02 wt%), total glycerine (0.24 wt%), and for water and sediment (0.05 wt%). An ethyl soy ester sample containing a high glycerine content (1.045 wt%) was prepared to investigate the effect of high glycerine on regulated emissions.

The acid number specification was generally met but there were some exceptions. The acid number specification is related to corrosion and small amounts of free fatty acids in esters should have no real impact on measured emissions during short-term test campaigns. The following fuels exceed the NBB specification for acid number: methyl stearate, blends of methyl linseed and methyl stearate, methyl and ethyl hydrogenated soy, ethyl soy, ethyl linseed, and oxidized ethyl soy. The stearate and hydrogenated soy fuels had high melting points and were extremely difficult to work with. Removal of free fatty acid from these fuels by neutralization was therefore not feasible. The reason for high acid number in the other fuels is less clear. Both the ethyl soy and oxidized ethyl soy were prepared by transesterification of methyl esters that meet the acid number specification. For the oxidized materials, peroxides may have decomposed upon heating yielding acids. A similar hypothesis may explain the high acid number of the ethyl linseed ester. Because several fuels do not meet the acid number specification, a methyl oleate with high acid number (10.1) was prepared. Emissions results for this fuel can be compared with results for a methyl oleate that meets the acid number specification.

The iodine number of the fuels ranged from 0.5 to 165. Iodine number is directly related to chemical structure as it measures the degree of chemical unsaturation of the ester fuels. Even though samples were prepared under argon and every precaution was taken to eliminate contact with air, analyses of the fuels showed the presence of peroxides. The tendency to oxidize is highly correlated with the iodine number of the fuel.

Table 8 shows GC/MS results (fatty acid speciation) for the fuels. No significant amounts of species with 8 through 11, 13, 15, 20, or 22+ carbon fatty acid chains were observed. The linoleate, laurate, and palmitate feedstock materials were relatively pure. Other feedstocks contain significant quantities of other fatty acids even though they were purchased as technical grade fatty acids. Only roughly 75% conversion was obtained in preparing ethyl soy and oxidized ethyl soy esters by transesterification of methyl esters.

The original plan was to produce very pure esters to test the hypothesis that the emissions of a biodiesel from a natural fat source could be quantitatively predicted by a linear combination of emissions from the individual fatty acids in the fat. While this is not possible with the esters produced, the wide variation in fuel fatty acid composition is adequate for us to analyze fuel effects by regression analysis.

Table 7. Analytical results for biodiesels prepared at CSM, note: M=methyl, E=ethyl.

Ester	Acid No.	Iodine No.	Peroxide No.	Glycerol Free/Bound	Water/Sediment	Cetane Number	Density, g/cm ³	Oxygen, wt%	Kinematic Viscosity	
									40°C	100°C
M-Oleate	0.13	90	162.2	0/0.022	0	56.0	0.8796	11.44	4.45	1.72
M-Oleate, high acid no.	10.1	84	369	0/0.023	0	--	--	--	--	--
M-Laurate	0.06	0.3	62	0/0.003	0	61.2	0.8730	14.68	2.46	1.07
M-Palmitate	0.16	0.5	77	0/0.011	0	--	0.8674	11.98	4.37	1.64
M-Stearate	1.9	0.5	74	0/0.035	0.005	--	0.8684	19.84	5.43	1.90
E-Oleate	0.19	79	184	0/0.035	0	--	--	--	--	--
E-Stearate	0.01	1	58	0/0.024	0	--	0.8636	10.84	5.14	1.88
M-Linseed for blending	0.4	--	--	0/0.132	--	--	--	--	--	--
M-Linseed/M-Stearate 2:1	1.62	116	295	0/0.032	0	--	--	--	--	--
M-Linseed/M-Stearate 1:2	2.5	66	387	0/0.024	0	--	--	--	--	--
Oxidized M-Soy	0.6	131	1861	0.001/0.012	0	55.0	0.8880	11.45	4.22	1.67
Oxidized E-Soy	3.81	118	210	0.001/0.021	0	46.2	0.8843	11.54	4.42	1.75
M-Linolenate	0.23	165	544	0/0.089	0	45.9	0.8941	11.25	3.99	1.64
M-Linoleate	0.41	151	148	0.001/0.126	0	41.7	0.8943	11.76	4.43	1.78
E-Linseed	2.9	157	21	0/0.041	0	43.4	0.8942	11.19	5.00	1.91
E-Linoleate	0.81	140	631	0/0.089	0	44.4	0.8869	11.05	4.98	1.81
M-Soy*	0.15	121	340	0.007/0.223	0	52.3	0.8836	11.44	4.03	1.64
E-Soy	3.02	122	123	0.003/0.031	0	47.3	0.8817	11.55	4.33	1.74
E-Soy, high glyceride	6.3	117	125	0/1.045	0	--				
M-Hydro-Soy	4.66	6	188	0.001/0.099	0	--	0.8688	11.10	5.73	2.01
E-Hydro-Soy	3.94	6	111	0/0.097	0	--	0.8643	6.52	5.82	2.06

Table 8. Results of GC-MS analysis of biodiesel samples for specific species.

Fuel	C12:0	C14:0	C14:1M	C16:0	C16:0 E	C16:1	C17:0	C18:0	C18:0 E	C18:1	C18:1 E	C18:2	C18:2 E	C18:3
<i>MW</i>	214.351	242.405	240.389	270.459	286.502	268.443	284.486	298.513	312.54	296.497	310.524	296.497	308.508	294.481
<i>Unsat</i>	0	0	1	0	0	1	0	0	0	1	1	2	2	3
E-Hydrogenated	0	0	0	11.900	0	0	0	88.100	0	0	0	0	0	0
E-Linoleate	0	0	0	2.7	0	0	0	2.4	0	6.4	0	88.5	0	0
E-Linseed	0	2.5	0	7.6	0	0	3.3	2.75	0	22.3	0	11.2	0	50.3
E-Oleate	0	3.1	0.3	6.7	0	4.2	4.6	2.5	0	58.1	0	9.1	0	9.1
E-Soy	0	0	0	5.2	8.8	0	0	6.1	2.86	10.6	13.7	18.59	34.12	0
E-Stearate	0	2.2	0	43.6	0	0	2.4	49.8	0	0.2	0	0.1	0	0
M-Hydrogenated	0	0	0	11.26	0	0	0	88.74	0	0	0	0	0	0
M-Laurate	99.2	0	0	0	0	0	0	0	0	0.6	0	0.2	0	0
M-Linoleate	0	0	0	1.4	0	0	0	0.7	0	5.2	0	86.5	0	6.16
M-Linolenate	0	0	0	7.4	0	0	0	3.7	0	24.8	0	2.9	0	61.2
M-Linseed:Methyl	0	0	0	20.8	0	0	0	28.65	0	15.18	0	7.59	0	27.78
M-Oleate	0	3	0.2	6.5	0	4.1	1.5	1.9	0	64.5	0	9.12	0	9
M-Oleate High	0	4.2	0.9	3.6	0	0	0	3.4	0	73.1	0	7.4	0	7.4
M-Palmitate	0.2	4.6	0	88.2	0	0	0.4	6.3	0	0	0	0	0	0
M-Soy	0	0	0	16.3	0	0	0	6	0	24.3	0	53.4	0	0
M-Stearate	0	1.3	0	42.1	0	0	1	52.6	0	0.9	0	2	0	0
M-Stearate:Methyl	0	0	0	38.59	0	0	0	44.06	0	4.81	0	2.41	0	10.14
Oxidized E-Soy	0	0	0	4.9	10.1	0	0	2.54	4.51	7.83	14.85	18.23	37.05	0
Oxidized M-Soy	0	0	0	15.2	0	0	0	5.3	0	22.5	0	57	0	0

Validation of Properties and Comparison with the Literature

Iodine Number:

Iodine number is an easily measured property that provides information on chemical composition. This property is measured by titrating the olefinic bonds in the fuel to establish the weight of iodine required to fully saturate the molecule. Figure 1 shows the relationship between measured iodine number by ASTM 5550 and the calculated iodine number from the GC/MS analyses. The agreement is excellent considering the accuracy of the speciation technique employed. The good agreement substantiates both the speciation results and measured iodine numbers.

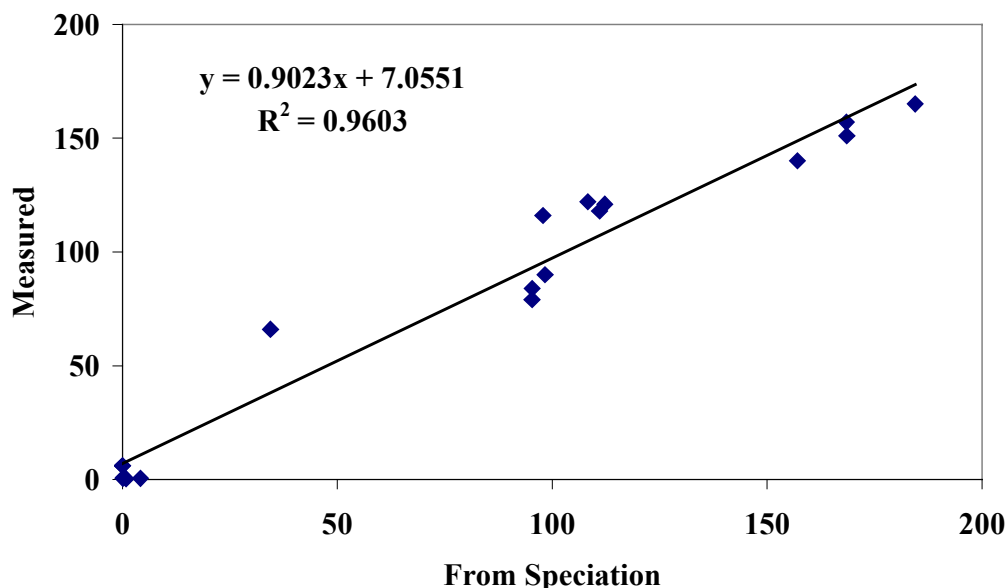


Figure 1. Comparison of measured iodine number with value calculated from fatty acid speciation data.

Density and Energy Density:

Since the biofuels all have very nearly the same carbon, hydrogen and oxygen contents, the gross and net heating values of each fuel per unit mass will be the same. Heating values for the IGT fuels as reported by us (CIFER) and IGT are compared statistically in Table 9. There is no difference in the reported average heating values at the 95% confidence level. Graboski and McCormick (1998) report the heating values of many methyl and ethyl esters. These are summarized in Table 10. Excluding ethyl tallow ester, the average HHV is 17,335 BTU/lb. For the suite of fuels produced in this test program, the average literature heating value is 176 to 249 BTU/lb greater than the IGT and CIFER reported heating values respectively. This is similar to the inter-laboratory variation of about 200 BTU/lb for this measurement. Thus, we conclude that heating values of the fuels produced here are consistent with those reported by previous researchers, and are not a function of biodiesel source so that the energy density per volume injected is directly proportional to the fuel density. Figure 2 compares measured density data for the test fuels with reported literature data (CRC, 1983). In general, the pair wise data agree well, substantiating the measurements obtained in this study.

Table 9. Comparison of heating values reported by CIFER and IGT.
t-Test: Two-Sample Assuming Equal Variances

	<i>CIFER</i>	<i>IGT</i>
Mean	17085.29	17161.86
Variance	5362.238	3288.143
Observations	7	7
Pooled Variance	4325.19	
Hypothesized Mean Difference	0	
df	12	
t Stat	-2.1782	
P(T<=t) two-tail	0.050055	
t Critical two-tail	2.178813	

Table 10. Gross heating values of various esters.

Ester	Number of Observations	Average GHV, Btu/lb
Methyl soy	9	17,355
Methyl rape	3	17,363
Methyl Tallow	3	17,283
Methyl Palm	1	17,271
Ethyl soy	1	17,208
Ethyl rape	1	17,433
Ethyl frying oil	1	17,428
Ethyl Tallow	1	17,940
Average ¹ (by fuel)	7	17,334

¹Ethyl tallow not included.

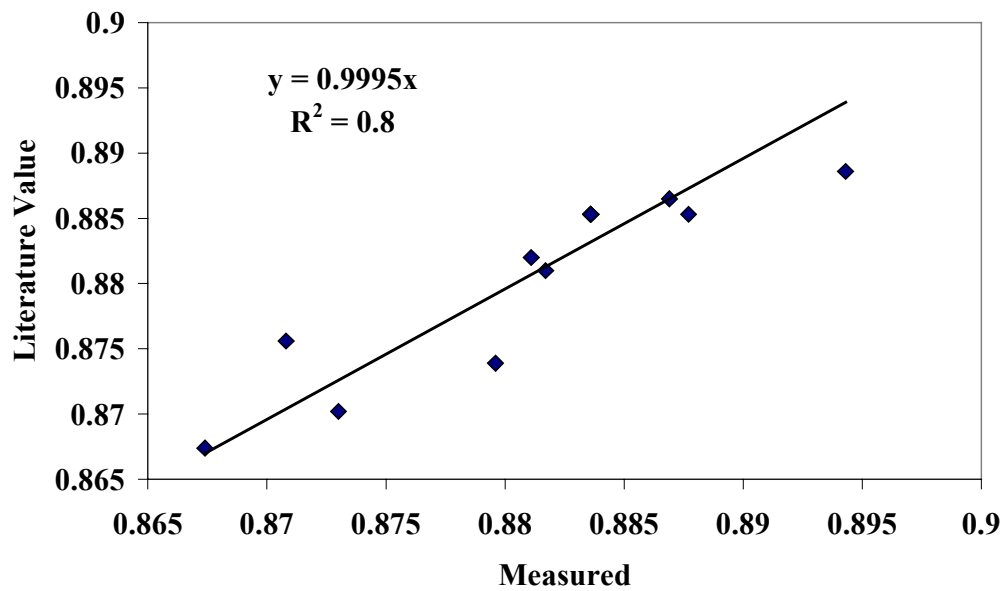


Figure 2. Parity plot for measured versus reported density.

Cetane Number:

The cetane number is a gross measure of ignition delay for fuel combustion. Figure 3 presents a parity plot for literature (Graboski and McCormick, 1998) and cetane number values measured in this study. The agreement is excellent except for methyl linolenate (22.7 versus 45.9 measured in this study). The ASTM D-976 test does not replicate cetane number well at both very low and very high values and thus this difference could be an experimental artifact. Based upon the trend for pure cetane number reported in the literature by Graboski and McCormick, the literature value is more likely to be correct for methyl linolenate.

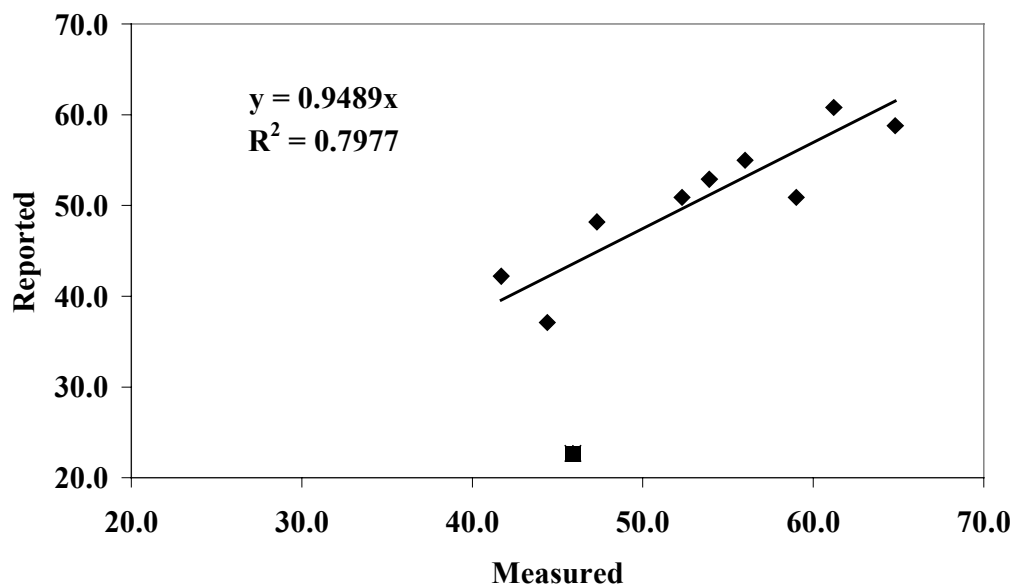


Figure 3. Parity plot for measured versus reported cetane number.

Viscosity at 40 °C:

The injection droplet size is dependent on a number of properties including viscosity and surface tension. Viscosity values are not available in the literature for pure esters at 40°C. Table 11 compares observations for esters made from fats for this program. Except for the IGT methyl soyate, agreement is excellent. It is concluded that the viscosity values measured by the analytical service labs are generally accurate.

Table 11. Comparison of measured viscosity with literature viscosity values (cs@40°C).

Ester	Measured	Literature
Methyl Soyate	4.03	4.08
Methyl Soyate IGT	4.55	4.08
Methyl Canola	4.63	4.83
Methyl Tallow	4.91	4.80
Ethyl Soyate	4.33	4.41

Results Part II: Certification Fuel Tests

The engine was initially mapped on certification diesel fuel and this map (run 4421) was used to generate the transient test for subsequent testing on all fuels. A plot of the torque map is shown in Appendix F. Each biodiesel testing sequence (a single fuel) was bracketed with at least two replicate tests on certification diesel. The fuel system was flushed before changing from biodiesel to certification diesel. Separate fuel filters were used for biodiesel and certification diesel to minimize cross contamination.

A common lot of certification diesel from Phillips Petroleum Co. was used throughout the test sequence (Lot D-434). Figure 4 shows all of the individual hot run NO_x and PM emissions from the certification diesel. All transient tests reported had passing statistics. The solid line represents the average emission of 4.59 g/BHP-hr for NO_x and the dashed line, 0.261 g/BHP-hr for PM.

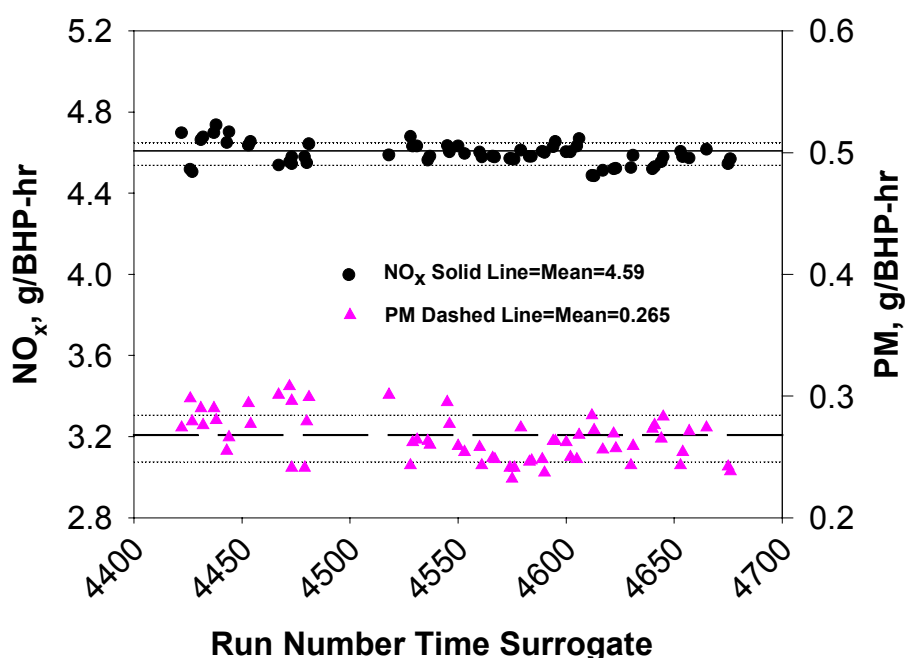


Figure 4. NO_x and PM emissions results for certification fuel runs performed over the study.

Tables 12 and 13 present descriptive statistics for the certification fuel runs. The median and mean are very close, suggesting a normal distribution and that the majority of the variance is due to random fluctuations in the data and not a large time series effect. During testing, the engine head cracked and needed to be replaced. The crack occurred between certification fuel runs 4454 and 4467. Between certification fuel runs 4481 and 4513 maintenance was performed on the engine dynamometer. Tables 14 and 15 compare NO_x and PM before run 4454 and after run 4513 using a t-Test to determine whether the two populations are the same. In both cases, we conclude that there was a small but statistically significant shift in emissions. However, we cannot conclude that the change is a result of mechanical effects as drift could produce a similar result.

Table 12. Descriptive statistics for daily average NO_x emissions from a 1991 DDC Series 60 engine using EPA certification diesel.

Mean	4.594
Standard Error	0.00629
Median	4.587
Standard Deviation	0.0533
Sample Variance	0.00285
Range	0.251
Minimum	4.485
Maximum	4.736
Count	72

Table 13. Descriptive statistics for daily average PM emissions from a 1991 DDC Series 60 engine using EPA certification diesel.

Mean	0.261
Standard Error	0.003
Median	0.258
Standard Deviation	0.019
Sample Variance	0.000
Range	0.086
Minimum	0.223
Maximum	0.309
Count	31

Table 14. Results of a t-test for pre- and post-head replacement for NO_x assuming equal variances.

	<i>Pre</i>	<i>Post</i>
Mean	4.641	4.587
Variance	0.005	0.002
Observations	13	51
Pooled Variance	0.00251	
Hypothesized Mean Difference	0	
Df	62	
t Stat	3.513	
P(T<=t) one-tail	0.000	
t Critical one-tail	1.670	
P(T<=t) two-tail	0.001	
t Critical two-tail	1.999	

Table 15. Results of a t-test for pre- and post-head replacement for PM assuming equal variances.

	<i>Pre</i>	<i>Post</i>
Mean	0.277	0.261
Variance	0.000	0.000
Observations	13	51
Pooled Variance	0.0003	
Hypothesized Mean Difference	0	
Df	62	
t Stat	2.828	
P(T<=t) one-tail	0.003	
t Critical one-tail	1.670	
P(T<=t) two-tail	0.006	
t Critical two-tail	1.999	

Engine Drift for NO_x

In order to analyze the effect of fuel composition on NO_x emissions, any bias due to engine drift on emissions needs to be quantified. Drift was examined in two ways. These were as follows:

- A Shewhart control chart (Mandel, 1964)
- Linear Regression Analysis

The purpose of the control chart is to judge whether a given time series data set of repeated measurements varies in a random fashion. Daily averages for EPA Certification Fuel data were formed and treated as individual observations. Following Mandel (1964), the data were then grouped into sets of three consecutive days and analyzed. Grouping smooths the time series plot and provides an estimate of the variance of the group averages. The results are shown in Figure 5. The “3 sigma” lines should include 99.7% (all) of the data if substantial bias or outliers are not present. Figure 5 shows the criteria is satisfied, but it is evident that a small downward drift in baseline NO_x occurred during testing.

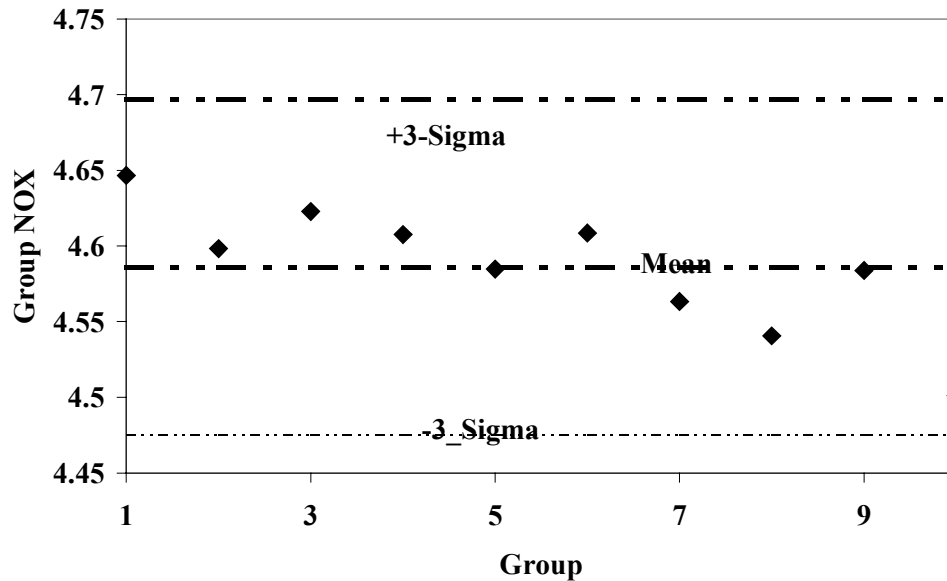


Figure 5. Shewhart means control plot for certification fuel NO_x emissions.

To attempt to quantify this drift, all data were regressed against run test number, which is a time surrogate. The regression results are shown in Table 16. The regression is highly significant, but it explains only 14% of the variation in the data. The residual plot (not presented) shows no trend suggesting that the majority of the variation is due to experimental uncertainty. The run numbers range from 4422 to 4676 for this test campaign. The smoothed certification NO_x values are thus 4.630 at the beginning and 4.561 at the conclusion of the campaign, suggesting a 1.5% total change in certification fuel NO_x emissions. Since this change is similar to the expected day to day variation in NO_x measurements, and on the order of the standard error for the regression, no correction to NO_x emissions data for engine drift seems warranted.

Table 16. Regression analysis for EPA certification fuel NO_x data.

<i>Regression Statistics</i>					
Adjusted R Square					0.1434
Standard Error					0.049
Observations					72

<i>ANOVA</i>					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.031	0.031	12.890	0.001
Residual	70	0.171	0.002		
Total	71	0.202			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	5.8365E+00	0.346	16.867	0.000
Run Number	-2.7279E-04	0.000	-3.590	0.001

Engine Drift for PM

As for NO_x, a Shewhart control plot, Figure 6, was developed for PM. While the data fall within the 3-sigma bands, there is a definite downward trend in PM with time. The PM data were regressed against run number and Table 17 shows a statistically significant result was obtained. The model explained only 19% of the variance; thus the variation is primarily due to experimental error. Based on run number, the mean PM ranges from 0.2818 g/bhp-hr at the start to 0.2510 g/bhp-hr at the end. This range exceeds the typical day-to-day variation of PM and thus a correction for PM drift might be warranted since the span is 11%. In the emissions data tables, all reported emissions are uncorrected for drift. In the fuel modeling section, NO_x is not corrected but PM is corrected using the equation in Table 17 relative to the mean PM for certification fuel.

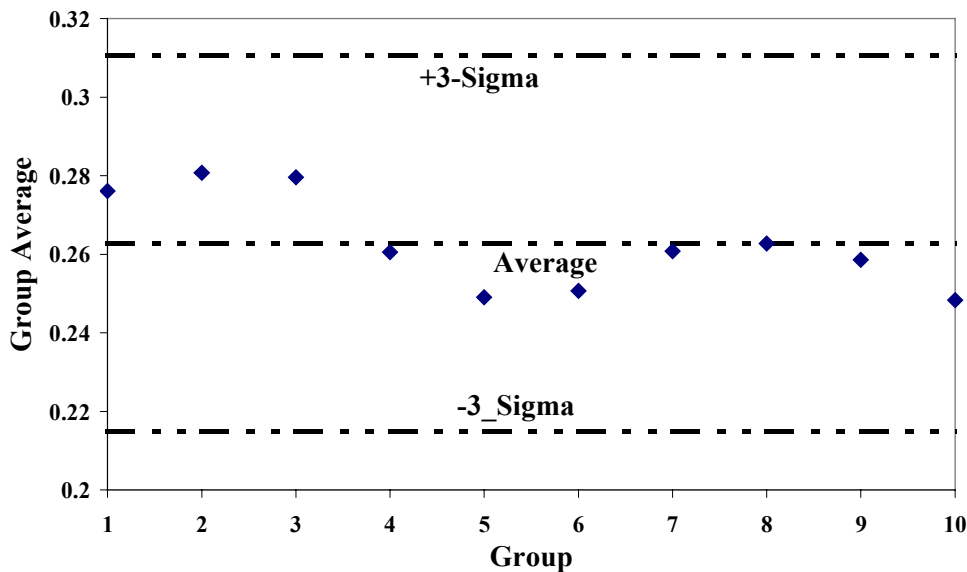


Figure 6. Shewhart means control plot for PM.

Table 17. Regression analysis for EPA certification fuel data for PM.

<i>Regression Statistics</i>					
		Adjusted R Square	0.192		
		Standard Error	0.018		
		Observations	72		

ANOVA					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.0062	0.0062	17.9139	0.0001
Residual	70	0.0241	0.0003		
Total	71	0.0302			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	8.1567E-01	0.130	6.279	0.000
Run Number	-1.2074E-04	0.000	-4.232	0.000

Significance of Results

Based upon these results, the raw emissions for the various biodiesels and their blends need to be corrected by only a small amount at most for PM and do not need to be corrected for NO_x. Thus, any statistical tests for significant changes in emissions between the certification fuel and individual biodiesels or between two biodiesels can be performed using the raw data for NO_x and either raw or corrected data for PM without compromising the analysis.

Results Part III: Emissions Testing of Biodiesels from Various Sources

The first section provides a brief test log indicating operability issues regarding certain fuels and maintenance performed on the engine during testing. The last two sections describe test results. All tests were run against the Number 2 diesel certification fuel map.

Test Log

The following observations were made during engine testing:

- 1/20/99 – Testing began
- 1/26/99 – Engine head cracked
- Ethyl oleate testing was lost due to water in the fuel resulting from the cracked engine head
- 2/4/99 – Dynamometer maintenance was conducted. The brushes were replaced and reseated.
- 3/18/99 – The ethyl linseed ester ran poorly. We found a small amount of water in the fuel. The variation in NO_x is high, but runs were not rejected. This could be due to the low cetane numbers of the tri-unsaturated fuels.
- 3/19/99 – The engine ran poorly on the 2:1 methyl stearate to methyl linseed ester. The fuel in the fuel lines froze during testing causing motoring during testing. The runs were rejected.
- 3/22/99 – Testing on the 1:2 methyl stearate to methyl linseed ester exhibited low fuel pressure most likely due to plugging in the fuel filter. There was minor motoring during testing, however the engine did run the test, and the statistics were acceptable. Thus, the runs were not rejected.
- 3/24/99 – The ethyl stearate ran poorly. There was no evidence of plugging or freezing of fuel lines. The statistics were acceptable and the runs were not rejected.
- 3/25/99 – We found traces of water in the ethyl soy ester. The water was most likely released from the drying agent and had no apparent impact on emissions data. The runs were accepted.
- 3/31/99 – There was sufficient fuel for only one transient test with methyl stearate.
- 4/2/99 – Fuel freezing with methyl hydrogenated soy ester was a problem. The second run was rejected because of very low cycle work.

Two of the IGT fuels were noted to be heterogeneous before emissions testing. The methyl lard contained about 1 cm of thick milky sludge on the bottom of the bucket. An attempt was made to homogenize by stirring; however, the two phases would not mix. After settling over night, the fuel was decanted off the top for testing. A noticeable film was present on the liquid. Inedible tallow also had a thick sludge on the bottom of the bucket, but in this case no attempt was made to mix the phases. The liquid was taken off the top of the sample and filtered before testing. Samples of the thick matter on the bottom of these two fuels were sent to Williams Laboratories for glycerine and water and sediment analysis. Both the methyl lard and methyl tallow had essentially zero free glycerine when analyzed by IGT (Appendix D), easily meeting the NBB specification. The retest on the methyl lard fuel showed water and sediment to be 0.6%, which exceeded the NBB standard by a factor of 10. Both fuels met the total glycerine standard of 0.24% maximum. The sludge on the bottom of the methyl lard bucket, on the other hand, contained 18% water and sediment. The methyl tallow sludge contained 3% water and sediment. If we assume the methyl lard sludge was made up 1% by volume of the bucket, the calculated water and sediment content for the completely homogenized fuel would be 0.18%, or more than 3 times the NBB standard.

In this program, every effort was made to hold to the proposed NBB fuel standard. Yet, problems

associated with water were evident indicating that the hygroscopic character of these esters can create problems during storage and transport. A second important observation is that flow problems are an issue with any fuel containing significant amounts of methyl stearate even at room temperature (the fuels were difficult to maintain in a liquid state). Methyl palmitate, which contains two fewer carbon atoms in the chain was tested with no problems, but would behave similarly at lower temperatures. When the fuel freezes, the engine must be motored by the dynamometer to hold speed and torque is lost. On the road, the vehicle would stall. Finally, fuels with a significant number of linolenic acid esters run poorly. This is probably due to the very low cetane numbers of these fuels. As data will show, linolenates also produce much more NO_x.

Fuels Produced from Various Waste Fatty Acid Streams

Regulated Emissions:

Average emissions results are presented in Table 18, along with the calculated coefficient of variation for repeated tests. Emissions results for all runs performed with these fuels are reported in Appendix G. The emissions results from the biodiesels and the B20 blends are also shown in Figure 7 for NO_x and PM.¹ The lines show the certification diesel average, in g/BHP-hr, for NO_x and PM. Examination of the results in Figure 7 indicates that PM reductions relative to certification diesel are, to a good approximation, dependent only upon the fuel oxygen content (roughly 2.5% for B20 blends and 12% for neat biodiesels). NO_x emissions appear to be different for biodiesels from different feedstocks.

A statistical analysis of the data was performed to allow a determination as to whether observed differences in NO_x or PM emissions relative to certification diesel are significant. This analysis employed a two sample t-test comparing certification fuel mean emissions with biodiesel mean emissions (hot start runs). The t-test tool in Microsoft Excel was used under the assumptions of equal variance, two tailed t-distribution, and a hypothesized mean difference of zero. A total of 81 certification fuel runs versus 3 biodiesel runs were used in each analysis for 82 degrees of freedom. Results are presented as p-value in Table 19, which provides an indication of the level of significance of any difference in mean emission values. For 20% methyl soyester the likelihood that NO_x increased relative to certification fuel is only 75%, thus it should be concluded that no significant change was observed. For neat methyl ester of edible tallow the observed NO_x increase is significant at the 91.5% confidence level. All other changes in NO_x are highly significant (96% at a minimum with many well above 99.9%). This includes the decrease in NO_x relative to certification fuel observed for the 20% methyl ester of inedible tallow blend. Changes in NO_x for the 20% blends are small. While there is no statistically valid reason to reject the data for the inedible tallow blend, common sense, and the fact the 100% inedible tallow methyl ester increases NO_x relative to certification diesel, suggest that this result be discounted. All PM changes are highly significant, and thus all biodiesel fuels reduced PM relative to certification diesel. Even the lowest significance level for 20% inedible tallow methyl ester is greater than 96%.

¹ Note that LFFA means low free fatty acid and HFFA means high free fatty acid.

Table 18. Average engine emissions data for various biodiesels and certification fuel.

Test Fuel		THC	NOx	CO	CO2	PM	VOF, % of	Fuel
		g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	PM	Economy
								btu/bhp-h
Cert Fuel/Lot D-434	Average	0.105	4.586	5.521	568	0.263	3.7%	7219
	CoV%	7.33%	2.37%	5.85%		4.39%	11%	
20% Methyl Soy/80% Cert	Average	0.113	4.627	4.854	567	0.221	4.3%	7433
	CoV%	1.21%	0.52%	0.90%		0.15%	33%	
20%LFFAG/80% Cert	Average	0.093	4.709	5.153	566	0.229	3.0%	7416
	CoV%	5.26%	0.22%	0.68%		3.32%	15%	
20%Inedible Tallow/80% Cert	Average	0.069	4.510	4.986	586	0.236	2.0%	7414
	CoV%	16.03%	0.34%	3.50%		1.86%		
Methyl Soy Ester IGT	Composite	0.076	5.323	3.509	579	0.083	21%	7337
	Hot Average	0.075	5.234	3.360	575	0.081	21%	7300
	CoV%	3.26%	0.20%	3.93%		4.31%	14%	
Methyl Canola/Lot 9777	Composite	0.069	5.178	3.129	572	0.081	18%	7090
	Hot Average	0.067	5.083	2.973	568	0.077	17%	7014
	CoV%	3.67%	0.22%	1.37%		4.75%	24%	
Methyl Lard/Lot 9811	Composite	0.077	4.765	2.660	585	0.072	26%	7495
	Hot Average	0.074	4.663	2.452	583	0.069	28%	7525
	CoV%	5.71%	2.24%	18.18%		6.07%	3%	
Inedible Tallow Lot 10996	Average	0.068	4.692	2.725	561	0.067	21%	7327
	CoV%	3.63%	0.07%	0.97%		4.53%	27%	
Edible Tallow Lot 112597	Composite	0.059	4.712	2.978	566	0.071	25%	7249
	Hot Average	0.060	4.647	2.858	562	0.070	25%	7195
	CoV%	2.91%	0.08%	1.56%		2.23%	18%	
Methyl LFFA Grease Ester	Composite	0.056	4.871	3.104	571	0.070	21%	7265
	Hot Average	0.054	4.809	2.990	567	0.068	20%	7213
	CoV%	2.34%	0.38%	2.19%		3.52%	15%	
Methyl HFFA Grease Ester	Hot Average	--	4.733	2.440	558	0.058	16%	7037
	CoV%		0.27%	2.41%		0.12%	17%	
Testing in February-May 2000:								
Cert Fuel/Lot D-434	Hot Average	0.055	4.640	4.606	559	0.232	6.1%	7341
	CoV%	3.29%	0.45%	3.51%	1.28%	6.03%	19.08%	
Methyl Soyester (Soyagold)	Hot Average	0.031	5.119	2.747	564	0.066	21%	7301
	CoV%	7.47%	1.10%	7.28%	0.08%	15.73%	11.33%	
Soapstock Methyl Ester	Hot Average	0.021	5.073	2.428	583	0.107	23%	
	CoV%	21%	1%	3%	0.5%	14%	5%	
Soapstock B20	Hot Average	0.034	4.715	4.528	569	0.184	12%	
	CoV%	22.05%	0.41%	2.21%	0.28%	5.35%	17%	

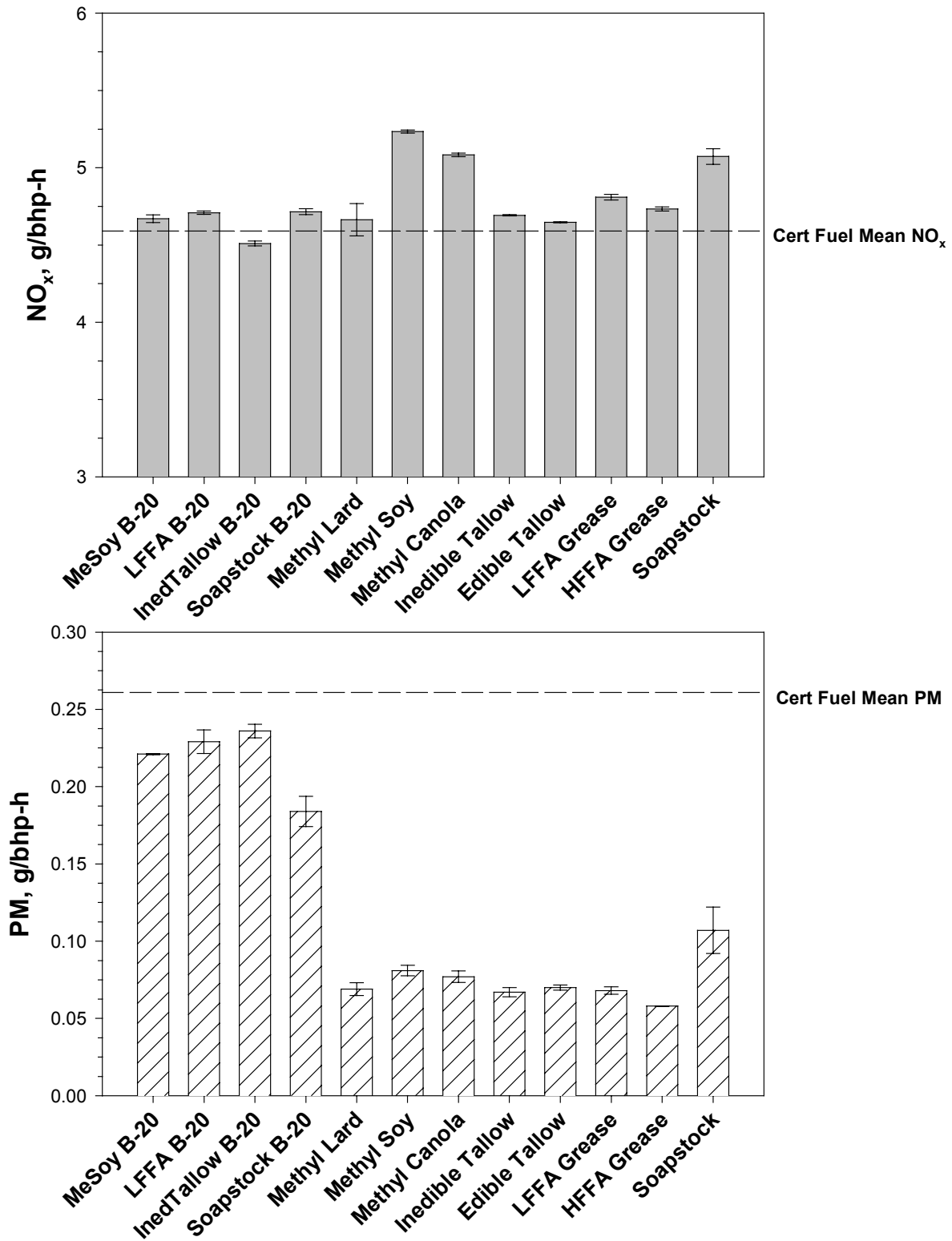


Figure 7. NO_x and PM results for testing of various neat biodiesel and B-20 blends.

Table 19. Results of statistical analysis of emissions testing data.

NO_x		
Fuel	Mean NO_x Emission	p-value
Certification diesel	4.586	--
20% Methyl Soyester	4.627	0.243474
20% LFFA Grease Ester	4.709	0.000747
20% Inedible Tallow Ester	4.510	0.035142
20% Soapstock Ester	4.715	0.000411
Neat Methy Soyester	5.234	6.61E-31
Neat Methyl Canola Ester	5.083	1.07E-23
Neat Methyl Lard Ester	4.663	0.037934
Neat Methyl Inedible Tallow Ester	4.691	0.003538
Neat Methyl Edible Tallow Ester	4.647	0.085153
Neat Methyl LFFA Grease Ester	4.809	1.19E-08
Neat Methyl HFFA Grease Ester	4.734	6.71E-05
Neat Methyl Soapstock Ester	5.073	3.05E-18
PM		
Fuel	Mean PM Emission	p-value
Certification diesel	0.263	--
20% Methyl Soyester	0.221	0.000981
20% LFFA Grease Ester	0.229	0.007793
20% Inedible Tallow Ester	0.236	0.03417
20% Soapstock Ester	0.184	9.21E-09
Neat Methy Soyester	0.0808	7.29E-25
Neat Methyl Canola Ester	0.0769	2.04E-25
Neat Methyl Lard Ester	0.0685	1.39E-26
Neat Methyl Inedible Tallow Ester	0.0665	7.2E-27
Neat Methyl Edible Tallow Ester	0.0697	1.99E-26
Neat Methyl LFFA Grease Ester	0.0682	1.22E-26
Neat Methyl HFFA Grease Ester	0.0576	4.32E-28
Neat Methyl Soapstock Ester	0.107	1.98E-16

Btu based fuel economy values from Table 18 are plotted versus run number in Figure 8 for both certification diesel and biodiesel runs. It is apparent from the figure, and from statistical analysis of the results, that there is no significant difference in fuel economy for the biodiesel fuels as compared to certification diesel.

Figure 9 presents a parity plot comparing cold start and hot start NO_x emissions. On average, NO_x increased by 0.53 g/bhp-h for cold starting of biodiesel fuels and 0.49 g/bhp-h for cold starting of certification fuel. While there is some variation in cold start NO_x emissions for the biodiesel fuels, there is no consistent trend. Figure 10 compares cold and hot start PM emissions in the same way. There is only a 0.02 g/bhp-hr increase in PM for biodiesel, but a 0.08 g/bhp-h increase for certification fuel.

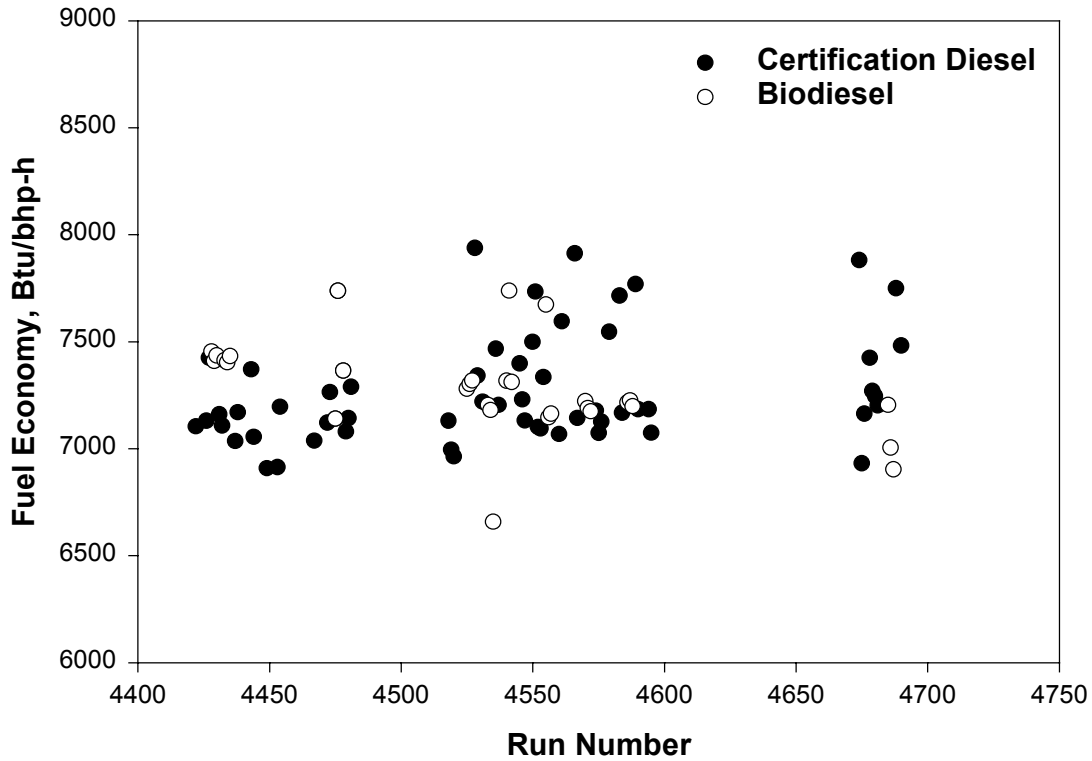


Figure 8. Btu based fuel economy comparison for certification diesel and biodiesel fuels.

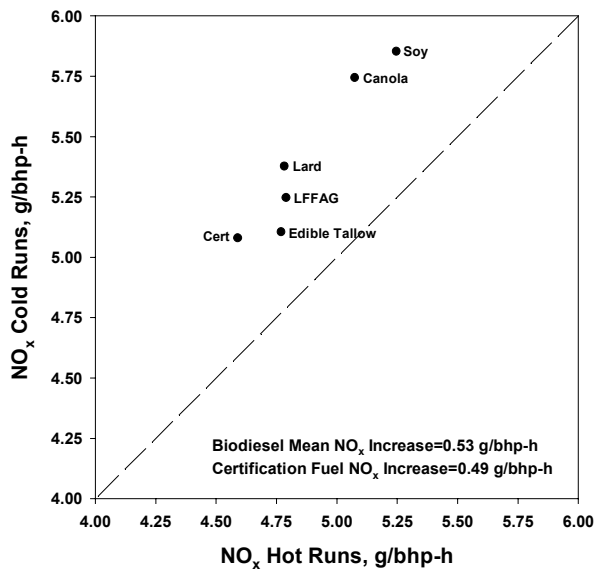


Figure 9. Comparison of hot start and cold start NO_x emissions.

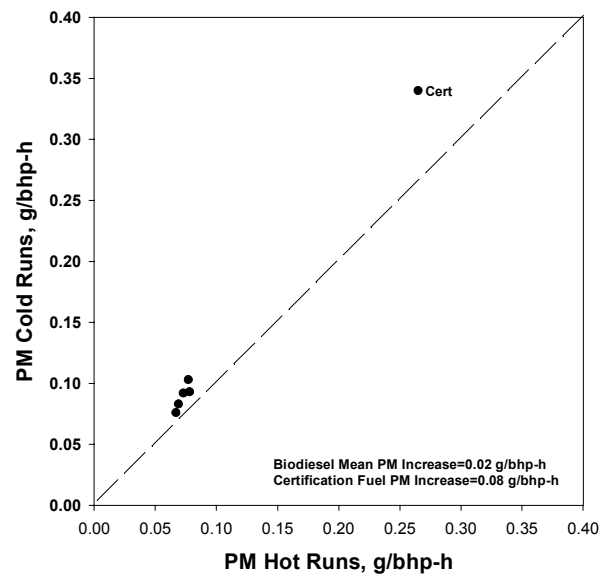


Figure 10. Comparison of hot start and cold start PM emissions.

Certification diesel (the same lot), methyl soyester, and the soapstock ester were tested in February 2000. The purpose of this testing was to repeat measurement of speciated gaseous hydrocarbon emissions, but the testing also provides an opportunity to confirm earlier test results. These tests are also reported in Table 18 as the final few entries. It is apparent that emissions from certification diesel and methyl soyester are confirmed in these additional tests.

Non-Regulated Emissions:

Volatile Organic Fraction: Table 18 reports the PM volatile organic fraction (VOF, similar to soluble organic fraction or SOF) for runs using certification diesel and several of the neat biodiesels. The VOF averages about 5.5% for certification diesel, but increases to an average of 21.4% for the neat biodiesel fuels combined. Results are also shown in Figure 11 where it can be seen that there are no obvious trends in the emissions in terms of biodiesel source material. Experimental error in VOF measurements is larger than error in PM measurements because a much smaller weight difference exists and a relatively large blank correction must be made.

The VOF emission for certification fuel (5.5% of 0.261 g/bhp-hr PM) is 0.0144 g/bhp-hr. For the biodiesels on average (21.4% of 0.07 g/bhp-hr), it is 0.0150 g/bhp-hr. The indicated B20 VOF levels are not consistent with the VOF for the certification fuels and neat biodiesel. With the exception of B20 soapstock, the indicated volatile emission for the B20 runs is lower than for certification fuel.

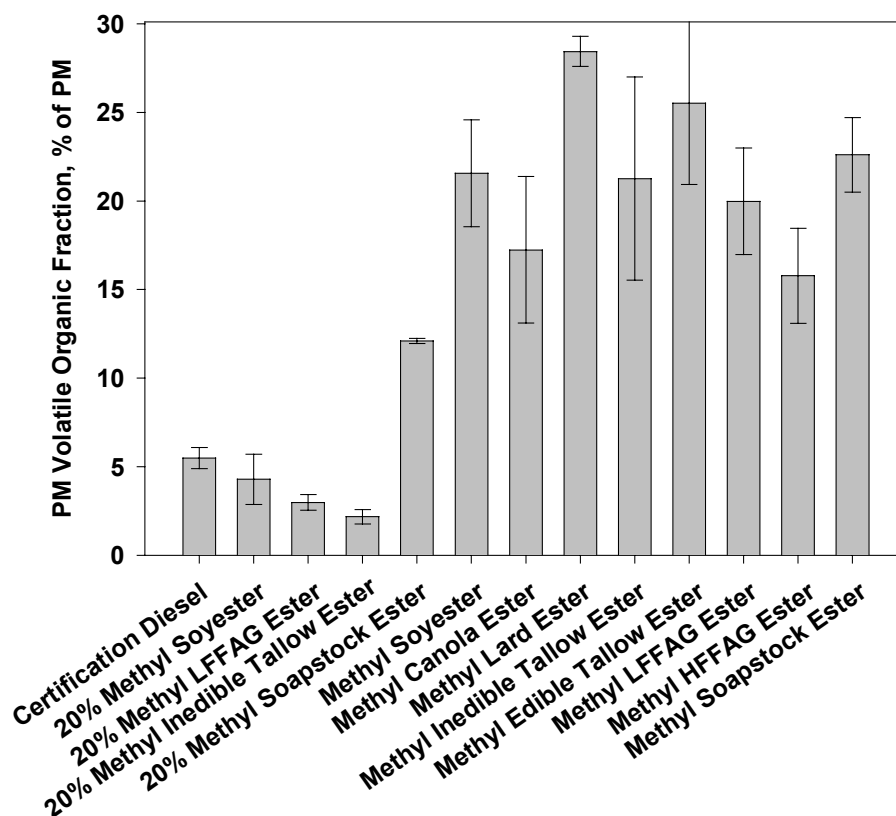


Figure 11. Volatile organic fraction emissions for hot start runs as a percent of total PM.

Sulfate Emissions: Table 20 reports sulfate emissions for selected fuels. Neat biodiesel contains no sulfur and so sulfate emissions are significantly less for these fuels. The residual sulfate can be attributed to emissions of lubricating oil. Sulfate comprises roughly 1%-2% of total PM for certification diesel. Because PM from fuel combustion is much lower for biodiesel, sulfate as a fraction of total PM is higher, in the 3%-4% range. As expected, there is no difference in the sulfate emission for biodiesel from different sources.

Table 20. Sulfate emissions results for selected fuels.

Run	Fuel	PM g/bhp-h	Sulfate g/bhp-h	Sulfate % PM
4517	Cert Fuel/Lot D-434	0.340	0.0043	1.26%
4518	Cert Fuel/Lot D-434	0.301	0.0043	1.42%
4519	Cert Fuel/Lot D-434	0.311	0.0043	1.38%
4520	Cert Fuel/Lot D-434	0.315	0.0043	1.37%
	Composite	0.313	0.0043	
	Hot Average	0.309	0.0043	
4524	Methyl Soy Ester IGT	0.093	0.0029	3.11%
4525	Methyl Soy Ester IGT	0.078	0.0029	3.71%
	Hot Average	0.081	0.0029	
4569	Edible Tallow Lot 112597	0.076	0.0029	3.81%
4571	Edible Tallow Lot 112597	0.071	0.0029	4.08%
	Hot Average	0.071	0.0029	

Aldehyde Emissions: Aldehyde analysis results are reported in Table 21. Total aldehyde emissions from a DDC Series 60 engine have been reported to be in the 30-40 mg/bhp-h range (Mitchell, et al., 1994). Levels observed in this study are around 20 mg/bhp-h. The study by Mitchell and coworkers analyzed for slightly different aldehydes than are reported in Table 20, however 75% or more of the observed aldehydes in that study were formaldehyde and acetaldehyde. The primary reason that aldehyde emissions are much lower in the work reported here is that we observe formaldehyde emissions on the order of 1 mg/bhp-h, while Mitchell observes emissions of more than 20 mg/bhp-h. Emissions of acetaldehyde and higher molecular weight species are in good agreement. Because the esters were made with methanol or ethanol, one would expect that the majority of the aldehyde emissions would be formaldehyde or acetaldehyde. Methyl esters of soy, canola, and edible tallow did not produce emissions of total aldehydes or specific aldehyde species that are significantly different from emissions from certification diesel. Methyl lard ester has higher total aldehydes because of higher propionaldehyde, and slightly higher acetaldehyde emissions. This could be caused by a higher free glycerine or glyceride content for this fuel, however analyses for these species reported by IGT (Appendix D) do not show a higher glyceride content for this fuel. The LFFAG methyl ester produced lower total aldehyde emissions than the other fuels, primarily because of lower propionaldehyde emissions. One can speculate that this fuel had exceptionally low levels of free and bound glycerine leading to the low emission of the C₃ aldehyde, however this is not supported by the glycerine analysis in Appendix D.

In general it seems reasonable to conclude that aldehyde emissions from various biodiesels are not significantly different than aldehyde emissions from certification diesel fuel. Smith and coworkers (1998) also observed no difference in aldehyde emissions between a biodiesel (hydrogenated soybean oil ethyl ester) and No. 2 diesel for a 1997 Caterpillar 3406E engine. Total aldehyde emissions in this study were roughly 30 mg/bhp-h, similar to the level reported here. Sharp tested soybean oil methyl ester in a 1997 Cummins N14 engine and found aldehyde emissions to be roughly 40 mg/bhp-h for the biodiesel

and 75 mg/bhp-h for No. 2 diesel. Thus all studies measure a similar level of aldehyde emissions and differences in conclusions regarding the effect of biodiesel on aldehyde emissions may be accounted for by differences in engine technology and testing procedures.

Table 21. Aldehyde emission results, mg/bhp-h.

Fuel		Formaldehyde	Acetaldehyde	Propionaldehyde	Hexanal	Heptanal	Octanal	Nonaldehyde	Decylaldehyde	Total Aldehydes
Certification Fuel	Composite	0.89	8.65	9.27	0.39	nd	nd	nd	0.78	20.0
	Hot Average	0.87	8.23	10.8	0.40	nd	nd	nd	0.47	20.8
Methyl Soyester	Composite	0.47	7.44	12.4	0.35	1.42	0.036	nd	0.58	22.7
	Hot Average	0.52	7.42	12.6	0.35	1.31	0.042	nd	0.62	22.9
Methyl Canola-ester	Composite	0.47	4.79	12.4	0.10	0.33	0.055	nd	0.47	18.6
	Hot Average	0.48	4.54	12.4	nd	0.39	0.064	nd	0.51	18.4
Methyl Lard Ester	Composite	0.62	8.58	18.0	nd	1.11	nd	nd	0.74	29.0
	Hot Average	0.63	8.91	18.9	nd	1.20	nd	nd	0.70	30.4
Edible Tallow Ester	Composite	--	--	--	--	--	--	--	--	--
	Hot Average	1.52	3.51	12.0	0.68	1.95	1.35	nd	0.41	21.4
LFFAG Ester	Composite	0.77	4.10	3.65	0.27	0.93	0.97	0.020	0.030	10.7
	Hot Average	0.85	3.47	Nd	0.27	0.95	0.91	0.024	nd	6.47

Emissions Testing of Pure or Nearly Pure Ester Fuels

Average emissions data for these fuels are listed in Table 22 and complete results are in Appendix H. Figure 12 summarizes results for methyl ester fuels and Figure 13 for ethyl ester fuels. With the exception of methyl palmitate, methyl laurate, methyl and ethyl stearate and the methyl and ethyl esters of hydrogenated soybean oil, all biodiesel fuels produced higher NO_x than certification diesel and all lowered PM relative to certification diesel. Thus, highly saturated fuels, those with no double bonds in the fatty acid chain, appear to have the lowest NO_x emissions. Examination of the series laurate, palmitate, and stearate (C12, C16, and C18) suggests that longer chain esters have lower NO_x emissions. The highest PM emissions were observed for methyl linoleate, which was the only biodiesel with PM emissions exceeding those of certification diesel.

Other Testing

Effect of Oxidation on Regulated Emissions:

Figure 14 shows the effect of oxidation on NO_x and PM emissions. The oxidized methyl soy ester was a sample that had been stored at the CIFER lab for several years and become oxidized at room temperature. The ethyl soy ester was prepared from this fuel by transesterification. Apparently heating during the transesterification process caused some of the peroxides in this sample to decompose, resulting in a lower peroxide number. From an emissions standpoint oxidation had no effect. Oxidation would be expected to raise the cetane number of the fuel slightly, however, the impact in this analysis was not observable.

Methyl and Ethyl Esters:

Data on the relative emissions performance for methyl versus ethyl esters is inconclusive. A comparison can be made based upon five fuels that were prepared using methanol or ethanol. Some of the fuels gave erratic emissions results and so this comparison is qualitative. The ethyl ester produced higher NO_x in 3 out of 5 tests compared to the methyl ester. While the absolute average difference was 3.6%, it is essentially all attributed to the oleate fuels. One can tentatively conclude that neat methyl and ethyl esters produced from the same base stock produce the same NO_x emissions. The ethyl oleate fuel gave a much higher PM but the ethyl linoleate fuel gave a much lower PM compared to the methyl fuel. The reason for the differences is not clear. Ethyl soyester PM emissions were 10.5% higher than methyl soyester emissions. Overall, we tentatively conclude that PM emissions from ethyl and methyl esters are similar or the same.

Table 22. Emissions testing results for biodiesels prepared from pure or nearly pure feedstocks.

		THC	Nox	CO	CO2	PM	Fuel Economy
Test Fuel		g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	btu/bhp-h
Cert Fuel/Lot D-434	Average	0.105	4.586	5.521	568	0.263	7219
	CoV%	7.33%	2.37%	5.85%		4.39%	
Methyl Linolenate	Average	0.071	5.643	3.605	582	0.186	8067
	CoV%	1.81%	0.06%	0.77%	0.49%	2.67%	
Methyl Oleate	Average	0.057	4.912	3.101	571	0.088	7945
	CoV%	11.02%	0.18%	1.98%	0.10%	3.37%	
Ethyl Oleate	Average	0.103	4.314	5.277	593	0.416	8305
	CoV%	2.94%	0.29%	17.76%	4.14%	33.92%	
Methyl Linoleate	Average	0.076	5.334	4.309	581	0.463	8125
	CoV%	0.31%	0.96%	2.51%	0.11%	3.87%	
Methyl Laurate	Average	0.106	4.573	2.073	573	0.044	8252
	CoV%	6.18%	0.07%	5.87%	0.07%	4.41%	
Soygold	Composite	0.072	5.331	3.223	574	0.076	8122
	Hot Average	0.068	5.245	3.070	569	0.073	8060
	CoV%	1.45%	1.27%	3.52%	0.61%	1.80%	
Oxidized Methyl Soy Ester	Hot Average	0.059	5.201	2.814	569	0.068	7986
	CoV%	18.71%	0.06%	0.54%	0.12%	1.92%	
Ethyl Linoleate	Hot Average	0.057	5.361	3.237	576	0.075	8417
	CoV%	1.30%	0.23%	0.27%	0.06%	2.80%	
Ethyl Linseed	Hot Average	0.040	5.144	3.802	549	0.137	6178
	CoV%	141.42%	4.90%	3.47%	8.58%	7.82%	
2:1 MeStearate:MeLinseed	15.780	0.846	4.571	8.490	596	1.890	7457
1:2 MeStearate:Me Linseed	Hot Average	0.079	4.779	3.149	584	0.176	7708
	CoV%	14.06%	1.51%	7.12%	0.78%	16.52%	
Ethyl Stearate	Hot Average	0.079	4.311	2.374	574	0.064	7937
	CoV%	10.87%	0.56%	1.33%	4.13%	10.18%	
Methyl Palmitate	Hot Average	0.046	4.311	2.186	563	0.060	8552
	CoV%	4.65%	0.56%	0.18%	0.32%	7.70%	
Ethyl Soy Ester	Hot Average	0.096	5.158	2.872	596	0.076	8093
	CoV%	3.42%	1.31%	6.49%	5.73%	13.75%	
High AN Methyl Oleate	Hot Average	0.046	4.844	2.859	574	0.076	8088
	CoV%	17.01%	0.49%	11.16%	0.13%	15.81%	
Ethyl Hydrogenated Soy	Hot Average	0.027	4.314	2.639	565	0.076	7837
	CoV%	119.79%	0.94%	5.31%	0.21%	3.61%	
Ethyl Oxidized Soy Ester	Hot Average	0.048	5.101	2.721	573	0.067	7924
	CoV%	3.42%	0.09%	6.76%	0.18%	3.55%	
High Glyc Ethyl Soy Ester	Hot Average	0.053	5.029	3.037	576	0.076	7994
	CoV%	8.39%	0.13%	1.96%	0.15%	4.77%	
Methyl Stearate	21.515	0.038	4.236	3.499	568	0.149	
Methyl Hydrogenated Soy	Hot Average	0.058	4.269	2.482	576	0.075	7925
	CoV%	37.62%	0.52%	11.93%	3.35%	5.93%	

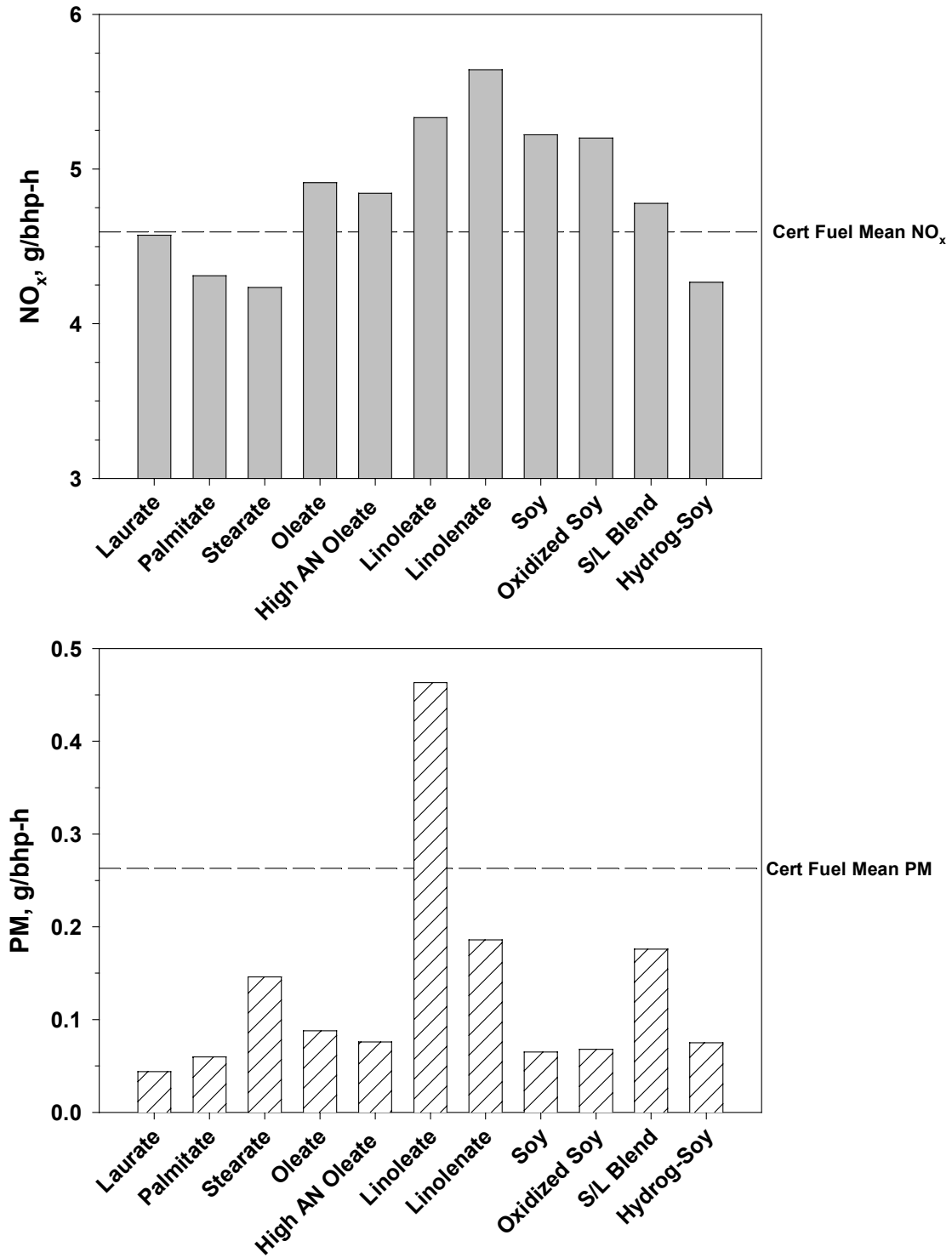


Figure 12. Summary of NO_x and PM results for methyl ester fuels.

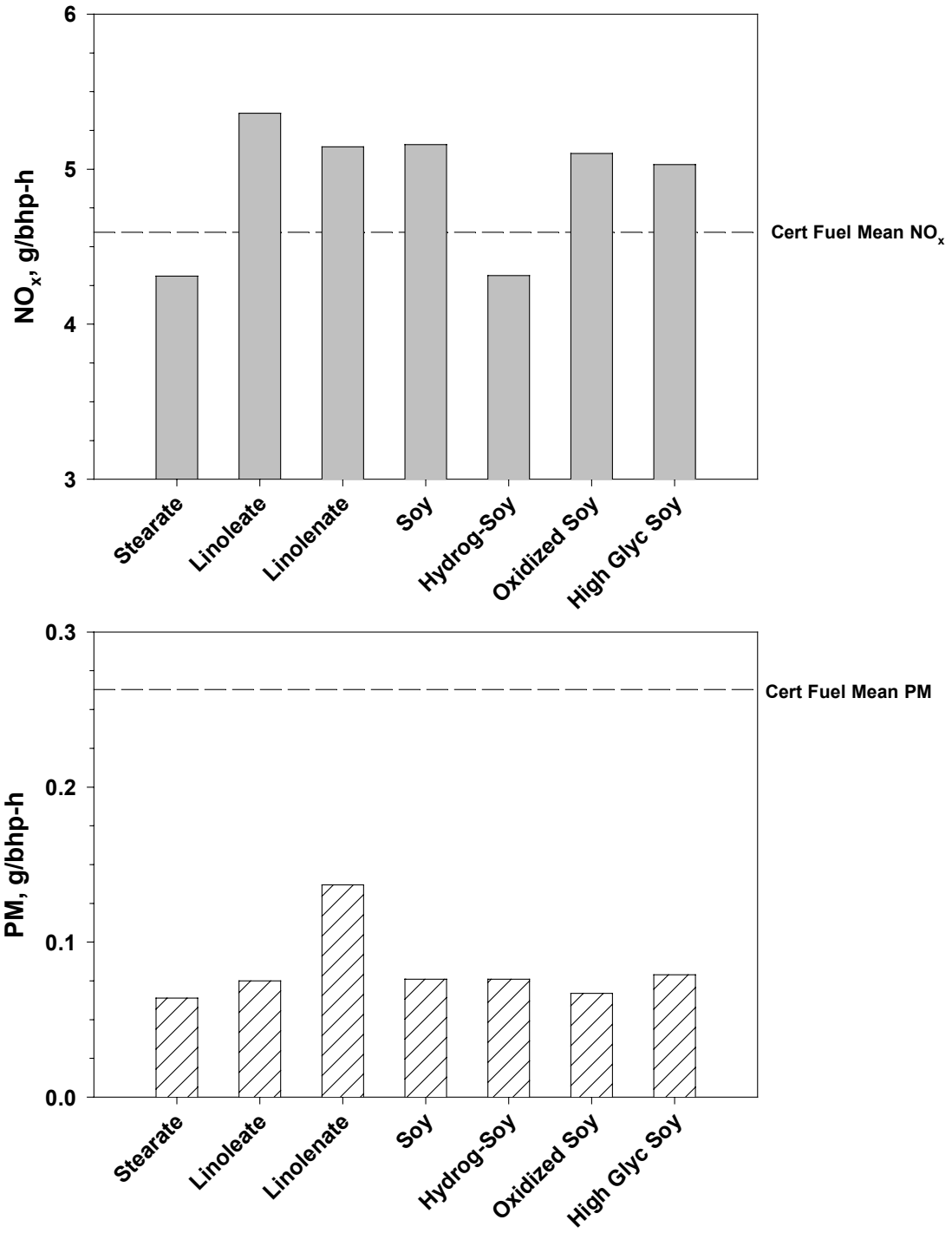


Figure 13. Summary of NO_x and PM results for ethyl ester fuels.

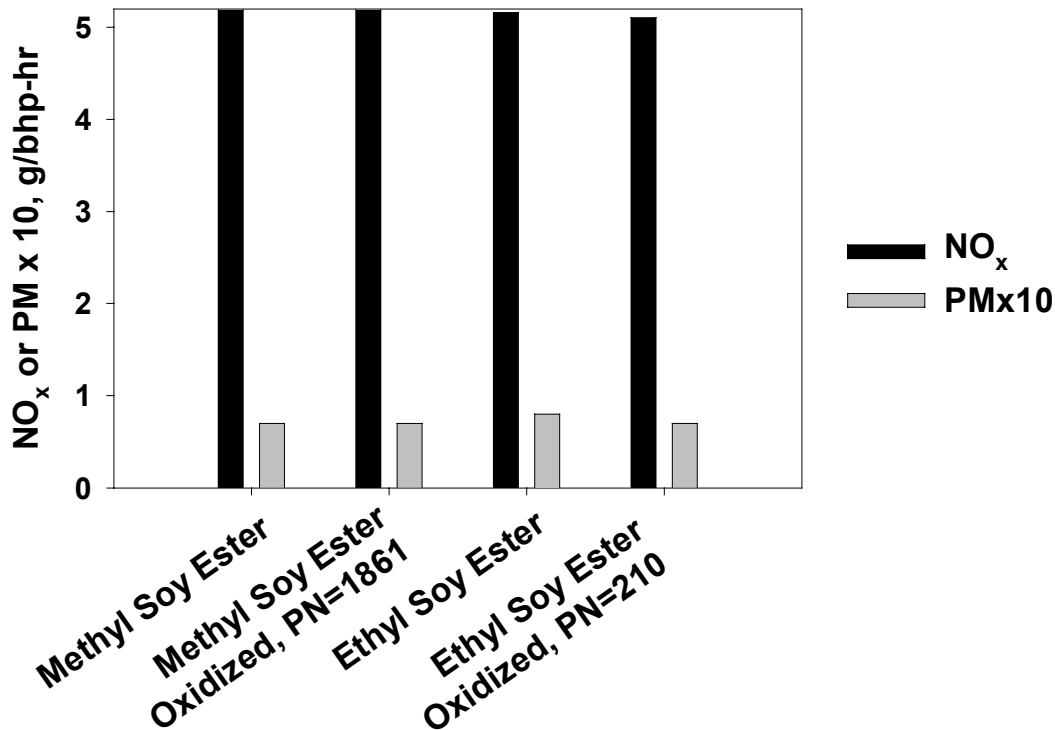


Figure 14. Effect of fuel oxidation on NO_x and PM emissions from methyl and ethyl soyesters, PN=Peroxide Number.

Out of Specification Impacts:

A number of the fuels tested did not meet the NBB specification for acid number. Figure 15 compares NO_x and PM emissions from methyl oleate fuels with both a high (10.1) and a low (passing) acid number. Both fuels gave identical emissions indicating that acid number has no effect on regulated emissions in short term emissions tests. Thus, we conclude that for emissions testing, the results reported for fuels with out of spec acid numbers are characteristic of the emissions that complying fuels would have produced.

To test the effect of glycerine content on emissions, two fuels were compared. These were ethyl soyate and a high glyceride ethyl soyate with 1.045% bound glycerine. The effect of the high glycerine content on PM emissions was not significant. However, the NO_x emission for the high glyceride fuel was 2.5% lower. Because the reference fuel measurements bracketing both fuels were consistent, we conclude that incomplete esterification of mono, di and triglycerides can result in lower NO_x emissions from the fuel. It has been reported that long term operation with such fuels can produce injector fouling problems. As we ran only a few tests with the high glyceride fuel, we observed no problems.

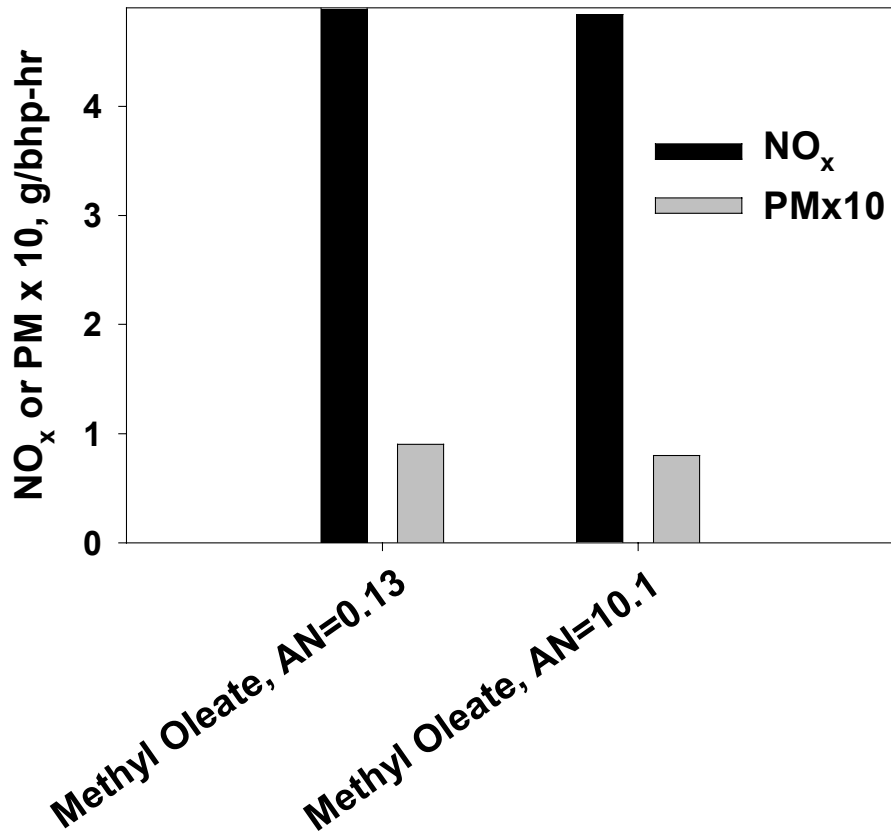


Figure 15. Comparison of NO_x and PM emissions for low and high acid number methyl oleate.

Defined Blends:

A goal of the program was to produce defined blends of stearate and linolenate esters to see if iodine number alone impacted the emissions. Four fuels were produced for this comparison:

- Methyl stearate
- 1 part methyl linseed, 2 parts methyl stearate to simulate methyl oleate
- 2 parts methyl linseed, 1 part methyl stearate to simulate methyl linoleate
- Methyl linolenate

Because of the unavailability of sufficient high purity linolenic acid, linseed oil was used to provide a high content of tri-unsaturated esters for the comparison. By omission, we did not test the methyl linseed ester alone which somewhat confounds our ability to analyze the results.

Both methyl stearate and the mixture of 1 methyl linseed with 2 methyl stearate could not be successfully run because of handling problems with the fuels. It was difficult to keep the fuels from solidifying in the fuel system due to the high pour point of methyl stearate.

The 2 parts methyl linseed/1 part methyl stearate blend was successfully run. It gave a NO_x emission which seemed to be less than a linear combination of the blending agents but a particulate emission more characteristic of the tri-unsaturate. Because of the uncertainty associated with handling and testing methyl stearate and its blends, we cannot draw strong conclusions regarding relationships

between emissions and additivity of double bonds. We do conclude that fuels which have flow problems (solidification of fuel during testing) do not have predictable behavior. Also, it appears that for PM, having a significant amount of tri-unsaturated esters in the fuels is a problem. Even though these fuels can produce PM emissions which are lower than certification fuel, they produce much higher PM than saturated, mono, and di unsaturated fuels.

Analysis Part I: Impact of Fuel Chemistry On NO_x and PM Emissions

The objective of this investigation is to determine the effect of biodiesel source material and ester molecular structure (number of double bonds and chain length) on pollutant emissions. These molecular structure parameters control fuel properties such as cetane number and density, as well as aspects of combustion chemistry.

Effect of Unsaturation in the Hydrocarbon Chain

The dataset includes a number of direct comparisons of fuels with differing numbers of double bonds in the fatty acid chain. These include both fuels prepared from pure or nearly pure fatty acids and fuels prepared from various, more practical, feedstocks. Figure 16 shows the effect of number of double bonds on NO_x and PM emissions from methyl and ethyl esters of nearly pure fatty acids. For NO_x emissions there is a highly linear relationship between increasing emissions and increasing number of double bonds. The range of NO_x emissions for the linolenate fuels (three double bonds) may be larger because of the low purity of these fuels, or the low cetane number (less than 30) which leads to poor engine performance. Importantly, the stearate based fuels with no double bonds produce significantly less NO_x than certification diesel. A fuel with an average of roughly 1.5 double bonds per molecule would be expected to be NO_x neutral relative to certification fuel. The number of double bonds has no consistent effect on PM emissions. Most biodiesels produced PM emissions of roughly 0.1 g/bhp-h independent of structure. The one exception is methyl linoleate which produced much higher PM of 0.48 g/bhp-h. This result is inconsistent with other testing results and is probably in error.

For fuels containing a mixture of molecules the iodine number is a measure of the degree of unsaturation or number of double bonds. Iodine number has been measured for the pure ester fuels and many of the fuels prepared from more practical feedstocks. Iodine numbers are also available in the literature for several of the other fuels. Table 23 presents iodine numbers for many of the fuels tested in this study. Figure 17 shows the relationship between iodine number and emissions of NO_x and PM, with emissions values for several specific fuels noted for reference. There is a highly linear relationship between iodine number and NO_x, and the regression predicts that a biodiesel with an iodine number of 38 will be NO_x neutral relative to certification diesel. PM emissions do not vary with iodine number.

While these data clearly show the effect of number of double bonds on NO_x emissions, the reason that this occurs remains open for speculation. It is possible that the double bonds participate in some combustion or pre-combustion chemistry to increase NO_x. It should also be noted that iodine number is highly inverse correlated with cetane number (high iodine number correlates with low cetane number), and cetane numbers were below 30 for the highest iodine number fuels tested in this study. Thus excessive ignition delay and poor combustion performance may also be proposed as a cause of the high NO_x. Density and isentropic bulk modulus are also effected by number of double bonds and might also be the cause. The important conclusion is that fuel chemistry is at the root of all of these fuel properties and the increased NO_x emissions observed for many biodiesel fuels.

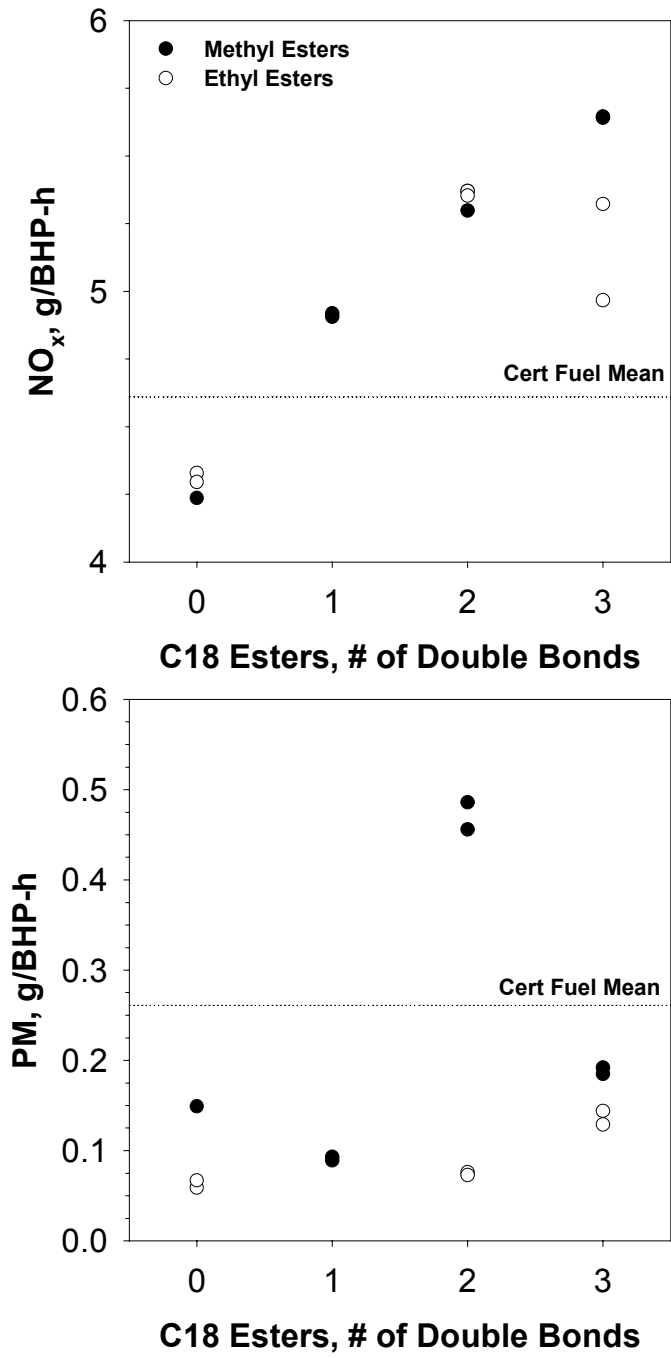


Figure 16. Effect of number of double bonds in the fatty acid chain on NO_x and PM emissions for pure ester fuels.

Table 23. Iodine number of fuels tested in this study.

Fuel	Iodine Number	Source
No. 2 Diesel	8	Graboski&McCormick, 1998
Ethyl Hydrogenated Soy	6	This work
Ethyl Linoleate	140	This work
Ethyl Linseed	157	This work
Ethyl Oleate	79	This work
Ethyl Soy Ester	122	This work
Ethyl Stearate	1	This work
Methyl Hydrogenated Soy	6	This work
Methyl Laurate	0.3	This work
Methyl Linoleate	151	This work
Methyl Linolenate	165	This work
Methyl Oleate	90	This work
Methyl Palmitate	0.5	This work
Soygold	121	This work
Methyl Stearate	0.5	This work
Ethyl Oxidized Soy Ester	118	This work
Oxidized Methyl Soy Ester	131	This work
Methyl Soy Ester IGT	133	Graboski&McCormick, 1998
Edible Tallow Lot 112597	64	Graboski&McCormick, 1998
Inedible Tallow Lot 10996	64	Graboski&McCormick, 1998
Methyl Canola/Lot 9777	97	Graboski&McCormick, 1998
20%Inedible Tallow/80% Cert	19	Calculated
20% Methyl Soy/80% Cert	33	Calculated
1:2 MeStearate:Me Linseed	66	This work
High AN Methyl Oleate	84	This work

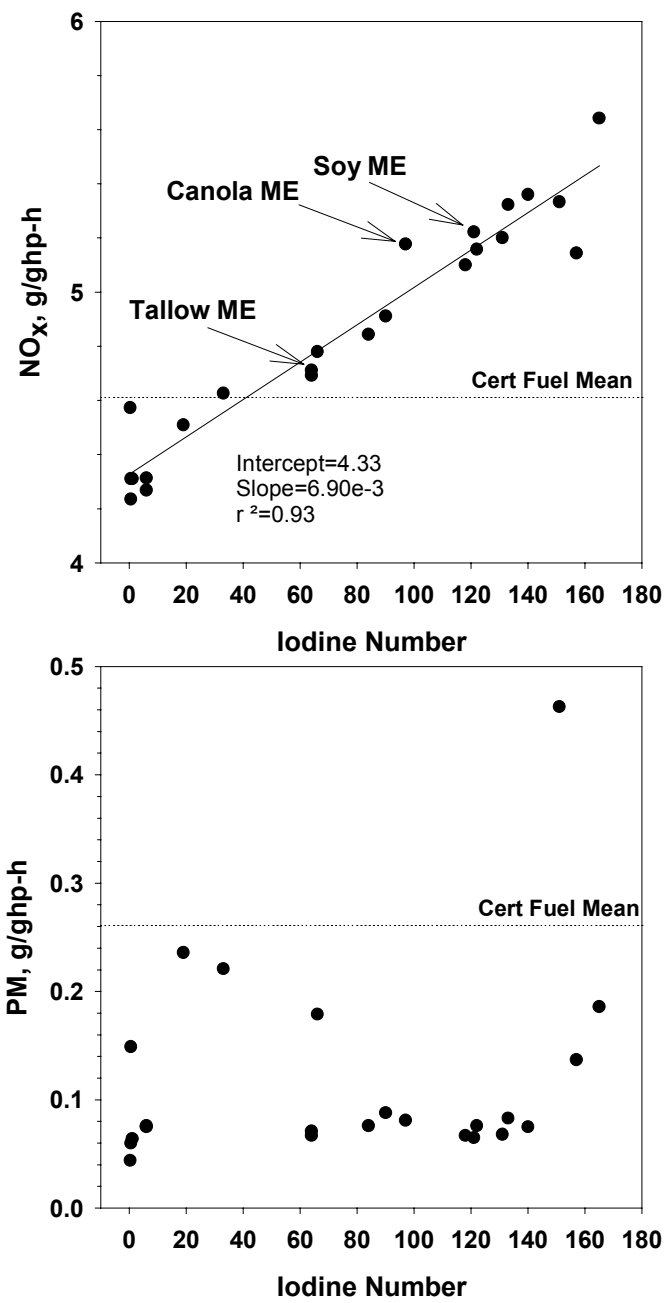


Figure 17. Effect of iodine number on emissions of NO_x and PM, data for all fuels tested in this study for which iodine number was available (see Table 23).

Effect of Hydrocarbon Chain Length

If all other factors are held constant (i.e. number of double bonds, etc), decreasing fatty acid chain length or molecular weight will lower boiling point and viscosity, and effect other fuel properties. One direct comparison of the impact of chain length on emissions was performed in this study. A series of saturated methyl esters based on lauric (C12), palmitic (C16), and stearic (C18) acids was prepared and tested. Ethyl stearate was also examined. This comparison is shown in Figure 18. Based on this evidence we conclude that shorter chain esters produce higher NO_x emissions, but note that the fully saturated methyl laurate (C12) still produced NO_x at or below the certification fuel level. Therefore shortening of the hydrocarbon chain may be a route to NO_x neutral fuels with improved properties. Chain length has no significant impact on PM emissions for this small dataset.

As for number of double bonds, chain length impacts a number of fuel properties including cetane number, density, and boiling point to name a few. Exactly how shortening chain length causes increasing NO_x remains a matter for speculation. But as before, the important conclusion is that fuel chemistry is at the root of all of these fuel properties. The most fundamental way to alter the emissions performance of a fuel is to alter fuel chemistry.

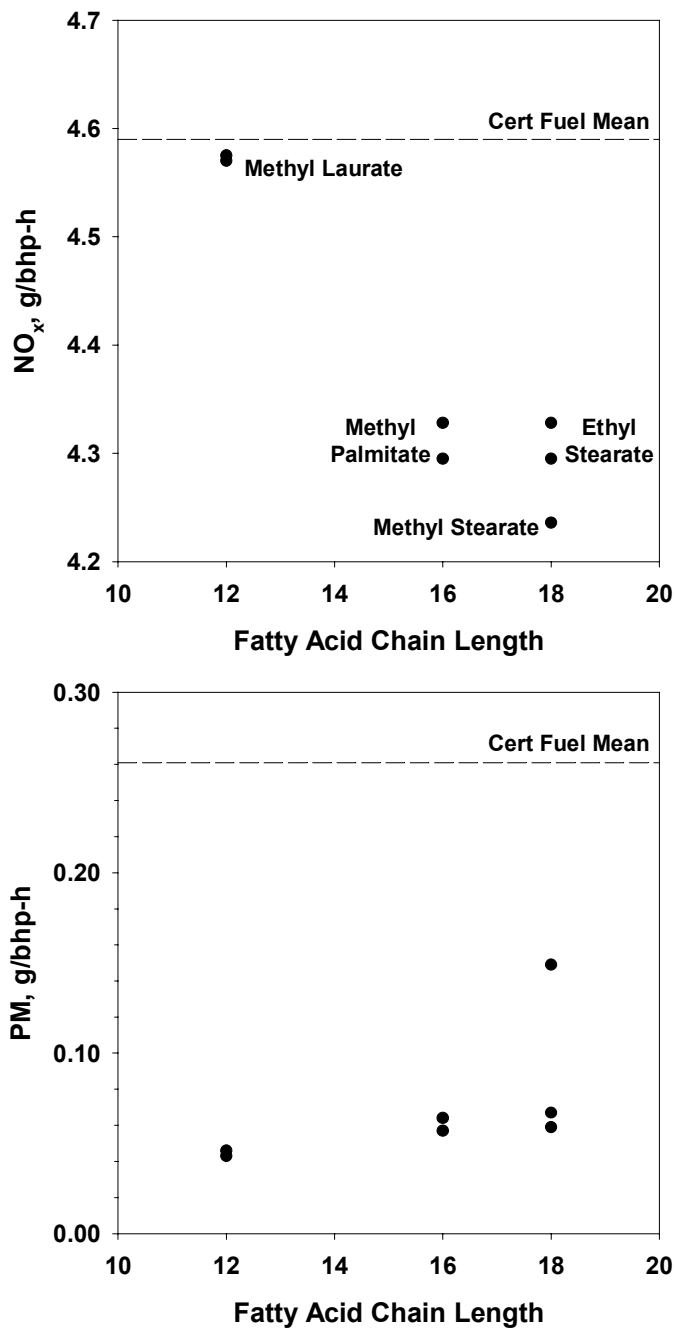


Figure 18. Effect of fatty acid chain length on NO_x and PM emissions.

Analysis Part II: Predictive Model of NO_x and PM Emissions Based on Fuel Properties

Physical Properties Data Base

The fuels were characterized by a variety of physical and chemical tests. While many are relevant to fuel specification, emissions are most likely to be dependent on properties which characterize molecular structure, energy density, ignition quality, and injection droplet size. Table 24 provides a summary of property data used for modeling.

Table 24. Fuel Property Data for Modeling.

Fuel	Cetane Number	Iodine Number	Density	Viscosity at 40°C	Oxygen weight %
Ethyl Hydrogenated Soy	NA	6	0.8643	5.82	6.52
Ethyl Linoleate	44.4	140	0.8869	4.98	11.05
Ethyl Linseed	NA	157	0.8942	5	11.19
Ethyl Oleate	53.9	79	NA	NA	NA
Ethyl Soy Ester	47.3	122	0.8817	4.33	11.55
Ethyl Stearate	76.8	1	0.8636	5.14	10.84
Methyl Hydrogenated Soy	NA	6	0.8688	5.73	11.1
Methyl Laurate	61.2	0.3	0.873	2.46	14.68
Methyl Linoleate	41.7	151	0.8943	4.43	11.76
Methyl Linolenate	45.9	165	0.8941	3.99	11.25
Methyl Oleate	56	90	0.8796	4.45	11.44
Methyl Palmitate	74.3	0.5	0.8674	4.37	11.98
Soygold	52.3	121	0.8836	4.03	11.44
Soygold	52.3	121	0.8836	4.03	11.44
Soygold	52.3	121	0.8836	4.03	11.44
Soygold	52.3	121	0.8836	4.03	11.44
Methyl Stearate	86.9	0.5	0.8684	5.43	19.84
Ethyl Oxidized Soy Ester	46.2	118	0.8843	4.42	11.54
Oxidized Methyl Soy Ester	55	131	0.888	4.22	11.45
Methyl Soy Ester IGT	47.2	NA	0.8877	4.546	11.16
Edible Tallow Lot 112597	62.9	NA	0.8708	4.908	11.74
Inedible Tallow Lot 10996	61.7	NA	0.8767	4.93	11.08
Methyl Canola/Lot 9777	55	NA	0.8811	4.63	11.04
Methyl Lard/Lot 9811	63.6	NA	0.8762	4.85	11.82
Methyl Yellow Grease	57.8	NA	0.8789	5.62	11.1
20%Inedible Tallow/80% Cert	NA	NA	NA	NA	2.73
20% Methyl Soy/80% Cert	NA	NA	NA	NA	2.52
20%LFFAG/80% Cert	NA	NA	NA	NA	2.31
HFFA Bio 3000	52.9	NA	0.8767	4.86	NA
1:2 MeStearate:Me Linseed	NA	66	NA	NA	NA
High AN Methyl Oleate	NA	84	NA	NA	NA
High Glyc Ethyl Soy Ester	NA	NA	NA	NA	NA

Iodine Number:

Iodine number is an easily measured property that provides information on chemical unsaturation of the fuel. Unsaturation can impact emissions. For example, free radical scavenging may be impacted by the number of olefinic bonds present.

Density and Energy Density:

Since the fuels all have very nearly the same carbon, hydrogen, and oxygen contents, the gross and net heating values of each fuel per unit mass will be the same. In the property chapter, it was concluded that the heating value is essentially the same for all biodiesels examined. Thus, the energy density per volume injected is directly proportional to the fuel density.

Cetane Number:

The cetane number is a gross measure of ignition delay for fuel combustion. If the cetane number is too low, the ignition will not occur at the time of injection and emissions and performance may deteriorate.

Viscosity at 40 °C:

The injection droplet size is dependent on a number of properties including viscosity and surface tension. It has been shown that droplet size can impact emissions due to poor distribution of fuel and increased burning times.

Property Relationships

Correlation coefficients between the various fuel properties were estimated for a group of 21 fuels for which measured or literature property values were available. These are shown in Table 25. Cetane number, density, and iodine number are all interrelated. Viscosity is weakly correlated with the other properties. This suggests that at most, two of these four variables should be used in a regression analysis.

Iodine number is not a good candidate as a correlating parameter because saturated molecules of different chain lengths all exhibit an iodine number of zero. Of cetane number and density, the latter is easiest and least expensive to measure and thus is a good correlating parameter. The selection of the correlating parameter does not suggest anything about the combustion mechanism.

Table 25. Correlation coefficients for several fuel properties.

	Cetane	Density	Viscosity	Iodine #
Cetane	1			
Density	-0.8974745	1		
Viscosity	0.4668638	-0.3292322	1	
Iodine #	-0.8967918	0.9583061	-0.2123165	1

Hot Test NO_x Emissions

In the following analysis, a correlation of hot transient test NO_x data is developed. Hot test emissions represent 6/7 of the total fuel emissions in a certification test. The effect of cold test emissions is small, nearly constant, and does not significantly impact the results reported here.

It has generally been reported that NO_x emissions are increased when biodiesel is substituted for conventional diesel. In this test program, EPA certification diesel was used to baseline the engine performance. Descriptive statistics for the baseline testing which bracketed biodiesel fuels during the test campaign are provided in Table 15. The NO_x emission with 95% confidence is 4.594± 0.0125 g/bhp-hr. For the biodiesel fuels tested, the NO_x emissions for the neat fuels ranged from 4.236 to 5.643 g/bhp-hr.

NO_x Modeling Results:

Figure 19 and Table 26 show a regression model for NO_x emission with density. The regression is highly significant and the single parameter explains 88% of the variance. Removing the ethyl linseed data point increases the R-square to 0.926. It was reported that the engine did not run well on ethyl linseed ester. Adding viscosity to the regression does not significantly improve the result. These relationships do not include petroleum diesel, which behaves differently.

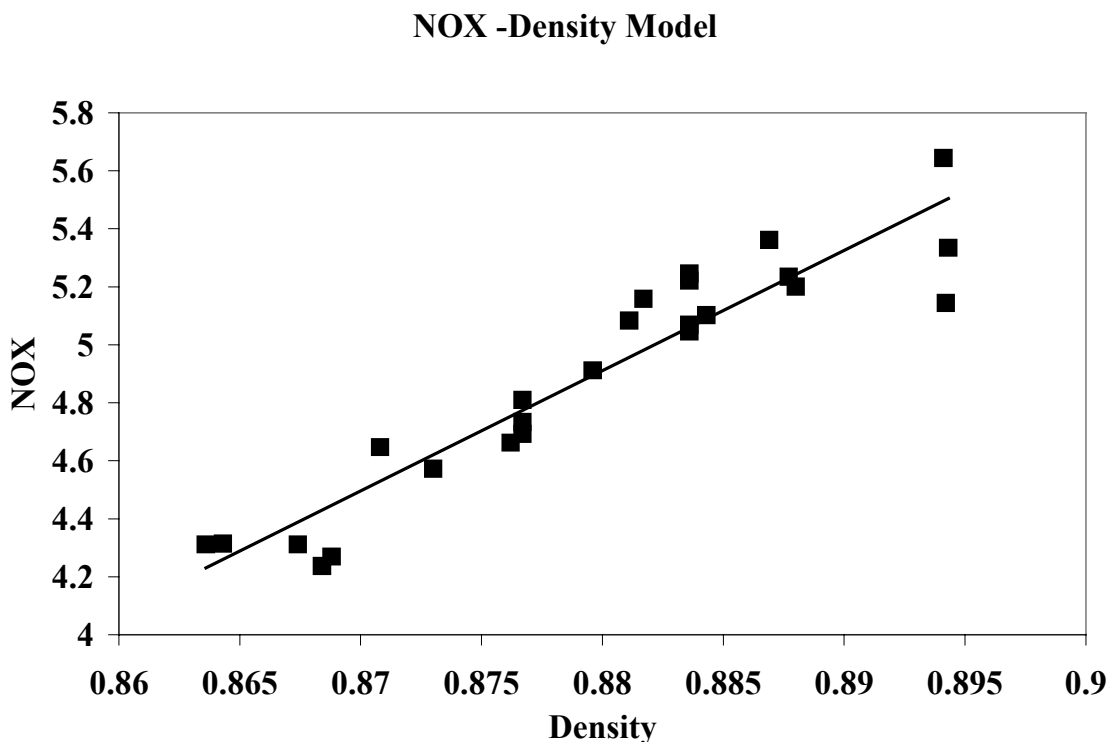


Figure 19. Relationship between density and NO_x emissions.

Table 26. Regression model for NO_x emissions with density.

<i>Regression Statistics</i>	
Adjusted R Square	0.8816
Standard Error	0.1371
Observations	25

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	3.377	3.377	179.762	0.000
Residual	23	0.432	0.019		
Total	24	3.809			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	-31.6139	2.7230	-11.6101	0.0000
Density	41.5055	3.0957	13.4075	0.0000

Hot Test Particulate Matter Emissions

Comparative Fuel Data:

Table 27 presents descriptive statistics for the PM data collected for EPA certification fuel. The 95% confidence limits suggest that the PM uncertainty is 5.5% of the average. PM values for the neat biodiesel samples range from 0.0443 for methyl laurate to 0.463 for methyl linoleate. Except for methyl linoleate, all neat biodiesel fuels reduced particulate emissions compared to Number 2 diesel.

Table 27. Descriptive statistics for daily average PM emissions with certification fuel.

Mean	0.261
Standard Error	0.003
Median	0.258
Standard Deviation	0.019
Sample Variance	0.000
Range	0.086
Minimum	0.223
Maximum	0.309
Count	31
Confidence Level (95.0%)	0.007

PM Modeling Results:

Figure 20 shows how corrected PM and density are related. It is evident that there is a critical fuel density where PM dramatically increases. Below that point, the PM emission is essentially constant and seemingly independent of the biodiesel source.

PM -Density Model

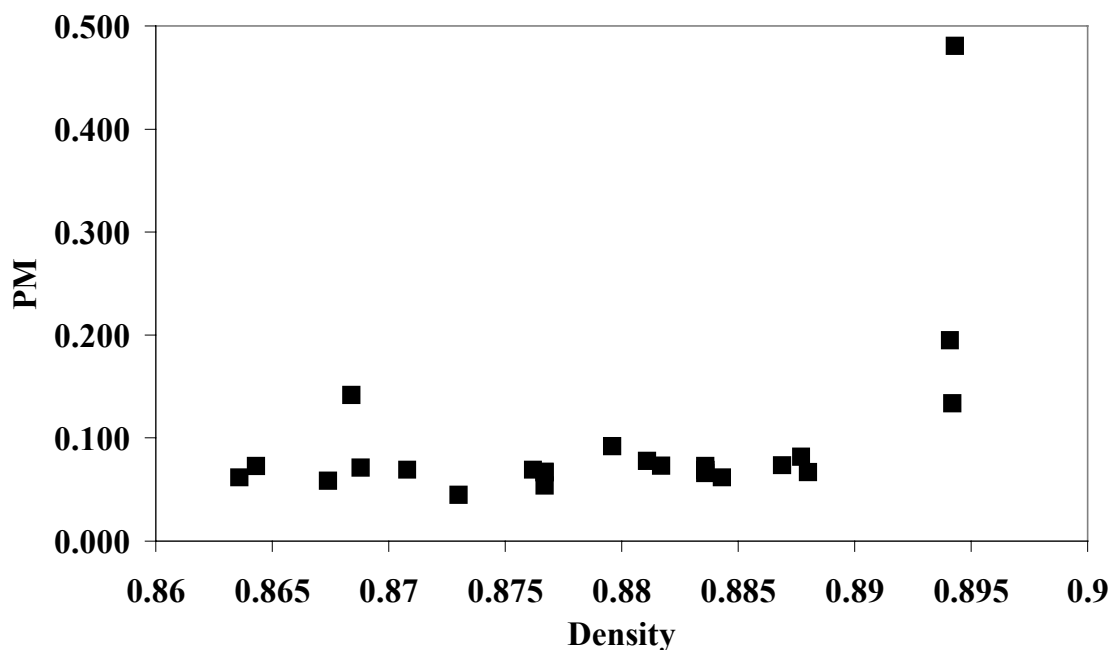


Figure 20. Relationship between fuel density and PM emissions.

To investigate whether the PM emissions are constant below the critical fuel density, a regression analysis was conducted with a data set modified by deleting the three fuels with a density above 0.89 plus methyl stearate. The PM emission for methyl stearate was high compared to other saturated esters, and this was probably related to difficulties in running the fuel. It had a pour point above room temperature and was very difficult to keep liquid during testing. The regression analysis results are given in Table 28. The regression as measured by the F-statistic is not significant. Further, the coefficients of the regression have significance levels of 0.2 and 0.3 suggesting that any variation in PM is likely due to chance. Assuming the model is significant, it predicts that PM changes 0.01 g/bhp-hr for density changes from 0.86 to 0.89. This difference is less than experimental error. Thus, we conclude that an adequate model for PM emissions from biodiesel fuels assumes constant PM of 0.070 g/bhp-hr, as given in Table 29.

Table 28. Regression model for biodiesel PM emissions with density.

<i>Regression Statistics</i>					
	Adjusted R Square				0.0510
	Standard Error				0.0094
	Observations				21

<i>ANOVA</i>					
	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	1	0.000	0.000	2.075	0.166
Residual	19	0.002	0.000		
Total	20	0.002			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	-0.2853	0.2455	-1.1618	0.2597
Density	0.4028	0.2796	1.4406	0.1660

Table 29. Final biodiesel PM model, fuel density less than 0.89 g/cc.

Mean	0.0695
Standard Error	0.0020
Median	0.0697
Standard Deviation	0.0090
Sample Variance	0.0001
Range	0.0435
Minimum	0.0443
Maximum	0.0877
Count	21
Confidence Level(95.0%)	0.0041

Blends

Data were collected for 20% blends of several biodiesel fuels with certification fuel. Figures 21 and 22 show how blending impacts emissions. Included in both figures are the data collected previously by the authors (Graboski, et al., 1996) with the same engine for methyl soy ester blends of 20%, 35%, and 65%.

NO_x Emissions:

The blending effect for the NO_x emissions is complicated and NO_x emissions do not appear to be simply related to the blend percentage as characterized by the oxygen level. At this time, there are insufficient data to develop a model for blends. Provisionally, one could estimate NO_x emissions by a linear combination of certification fuel NO_x and neat ester NO_x. For 20% blends such an estimate would seem to be conservative.

PM Emissions:

Figure 21 shows the PM response to blending for this study and previous testing. Between 1996 and present, there was a small shift in measured PM emissions of approximately 0.022 g/bhp-hr for certification fuel. However, the slope of the PM versus oxygen regressions for this work and the 1996 work are essentially identical. The data from the two test programs were regressed simultaneously with the addition of an intercept variable to represent the test program. Table 30 presents the results. The

model is highly significant and explains 99.35% of the variance. The PM slope is -0.0175 g/bhp-hr per percent oxygen in the fuel regardless of the biodiesel blended with the certification fuel. This supports the conclusion that for biodiesels with a density of less than 0.89, PM emissions depend only on the oxygen content.

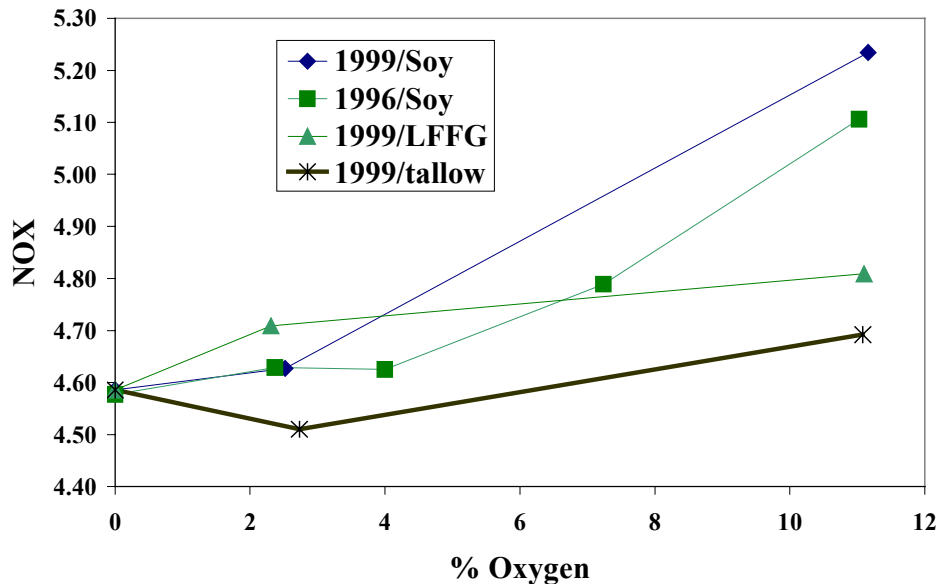


Figure 21. Effect of fuel oxygen content on NO_x emissions for several blends of biodiesel and certification diesel (1999 results from this study, 1996 results from Graboski, et al, 1996).

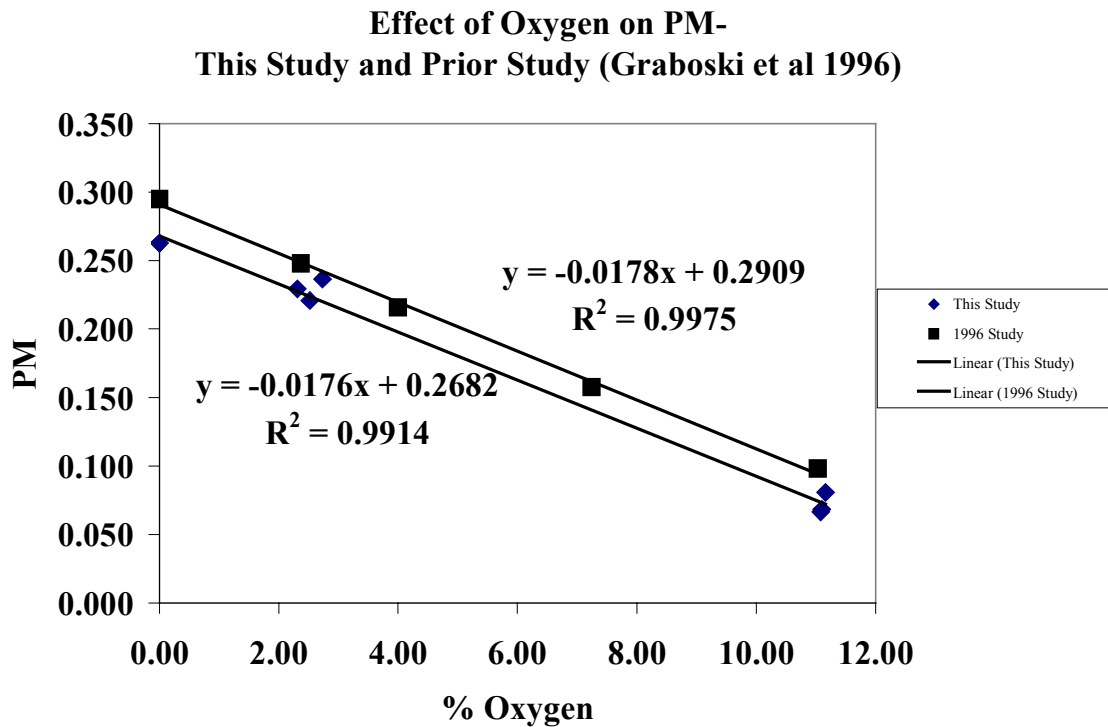


Figure 22. Regression model showing effect of oxygen on particulate matter.

Table 30. Regression model for the effect of oxygen on particulate matter.

<i>Regression Statistics</i>	
Adjusted R Square	0.9922
Standard Error	0.0072
Observations	14

ANOVA

	<i>df</i>	<i>SS</i>	<i>MS</i>	<i>F</i>	<i>Significance F</i>
Regression	2	0.086	0.043	826.080	0.000
Residual	11	0.001	0.000		
Total	13	0.087			

	<i>Coefficients</i>	<i>Standard Error</i>	<i>t Stat</i>	<i>P-value</i>
Intercept	0.2895	0.0039	74.6950	0.0000
% Oxygen	-0.0175	0.0004	-40.4717	0.0000
Test program	-0.0219	0.0040	-5.4327	0.0002

Discussion

This discussion is not dependent on whether pure esters or natural mixtures are considered. The correlation analysis described above treated mixed and pure esters simultaneously.

While density was used as the correlation parameter, this does not mean that varying energy density is the primary explanation for the NO_x variation. Figure 23 shows how cetane number and density are related. As Table 25 demonstrated, there is a near perfect correlation between these properties for biodiesels. Cetane number can be used to discuss emissions effects and the relationship between cetane number and emissions is shown in Figure 24. The regression shown in Figure 24 indicates that a NO_x neutral biodiesel would have a cetane number of 68. In order to get the full PM benefit, the cetane number of the biodiesel needs to exceed about 45. PM appears to be impacted only at cetane number values less than those of conventional diesel fuels today.

The impact of molecular structure is implicit in either the density or cetane number. More saturated esters have higher cetane numbers and lower densities than less saturated esters. Thus, the lower the iodine number, the lower the NO_x emission. Data collected also demonstrate the effect of chain length. The density of shorter chain length saturated esters is greater than longer chain saturated esters and therefore the NO_x emission is greater. However, methyl laurate with cetane number 61.2 and density 0.873 is NO_x neutral compared to certification fuel.

The results presented here are engine specific. Other engines and calibrations will probably give similar results but the impact of the NO_x/PM tradeoff for a specific diesel engine will change the overall results but probably not the trends. For a more detailed discussion of engine effects see Graboski and McCormick, 1998.

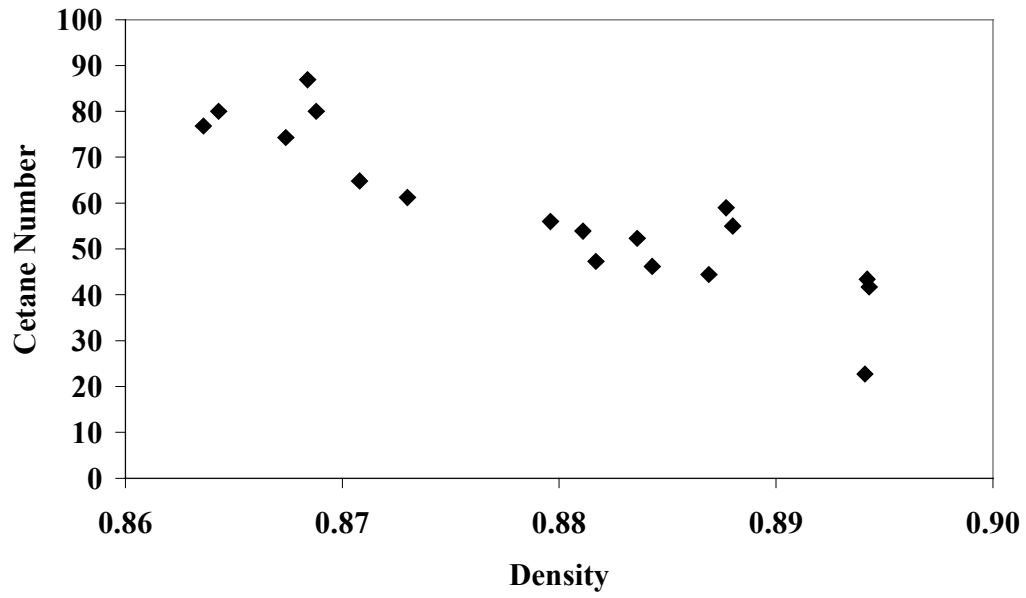


Figure 23. Relationship between cetane number and density.

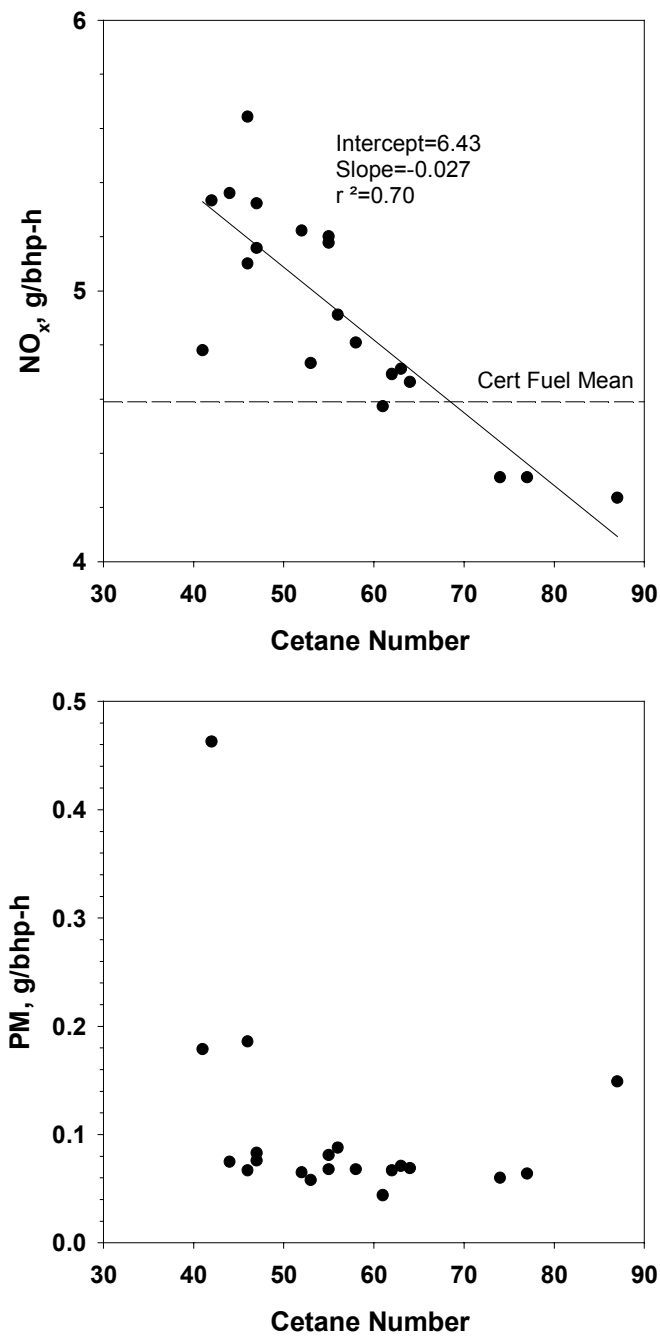


Figure 24. Effect of cetane number on NO_x and PM emissions. Cetane number data from this study and reported in the literature (Graboski and McCormick, 1998).

Conclusions

The emissions of NO_x and PM for a large number of neat biodiesel fuels of varying chemical composition measured using a 1991 DDC Series 60 engine can be correlated in a relatively simple fashion. The NO_x emission is highly correlated with the biodiesel density or cetane number. The PM emission for neat biodiesels is constant as long as the density is below 0.89 or the cetane number is above 45.

Based upon the neat biodiesel as characterized by the density or cetane number, the NO_x emission may be higher or lower than that for certification fuel. As long as the neat biodiesel has a density below the critical density of about 0.89, the PM emission will always be lower than that for diesel fuel.

The NO_x behavior of biodiesel blends is complex. Insufficient physical property data are available to characterize the effect of blending at this time, although provisionally for 25 blends a linear combination of NO_x emissions seems appropriate.

The effect of oxygen on particulate matter is well characterized by considering only the oxygen content of the blend. This conclusion appears to be robust.

Conclusions

Regulated emissions for hot and cold start tests for biodiesel produced from various feedstocks, as well as results for certain non-regulated pollutants, have been acquired. To understand the impact of biodiesel composition on emissions, the testing included a series of fuels consisting of pure or nearly pure fatty acid esters. A detailed analysis of the data was performed in an effort to determine what fuel properties are correlated with the increase in NO_x emissions observed for biodiesel here, and in most previous studies.

In total, 28 neat biodiesels and 4 B-20 blends were tested. Fuels were analyzed for a wide range of properties including water and sediment, free and total glycerine, iodine number, peroxide value, acid number, cetane number, density, kinematic viscosity, gross heating value, and carbon, hydrogen, and oxygen content. The specific fatty acid esters present in the fuels were also determined by GC/MS analysis. Regulated pollutant emissions, along with certain non-regulated pollutants, were measured on a 1991 DDC Series 60 engine via the heavy-duty transient test (40 CFR Part 86 Subpart N). Emissions from biodiesel fuels were bracketed with emissions measured for EPA certification diesel. This allowed comparison with a conventional diesel, and more importantly a measure of engine drift. Volatile organic fraction, PM sulfate, and emissions of certain aldehydes were also measured for many of the fuels. Samples for biological activity analysis by the University of California at Davis were collected.

All fuels prepared at CSM met the water and sediment specifications as well as the free and total glycerine specifications (with the exception of one fuel produced with high glycerine value on purpose). Not all fuels met the acid number specification, in particular fuels with a high stearate content as these were not liquid at or near room temperature making acid removal difficult. Fuels prepared by IGT met the water and sediment specifications immediately after synthesis. However, problems associated with water were evident when the fuels were received at CSM indicating that the hygroscopic character of these esters can create problems during storage and transport. Other properties are generally in good agreement with literature values.

Certification fuel runs exhibited a mean NO_x emission level of 4.59 g/bhp-h (+/-0.053) with no significant drift over the 4-month test program. PM emissions averaged 0.261 g/bhp-h (+/-0.019). A small downward drift in PM emissions was evident (11% of the course of the project). Thus, no correction for drift was applied to the NO_x emissions data but a correction was applied to the PM data.

For biodiesels prepared from a variety of real-world feedstocks, PM reductions relative to certification diesel are, to a good approximation, dependent only upon the fuel oxygen content (roughly 2.5% for B20 blends and 12% for neat biodiesels). NO_x emissions appear to be different for biodiesels from different feedstocks. All neat biodiesels increased NO_x emissions relative to certification fuel. In particular, feedstocks containing unsaturated fatty acid chains (soy, canola and soapstock) produce significantly higher NO_x emissions than more saturated materials. For the suite of biodiesels prepared from nearly pure fatty acids, all biodiesel fuels produced higher NO_x than certification diesel with the following exceptions: methyl palmitate, methyl laurate, ethyl stearate, and the ethyl ester of hydrogenated soybean oil. All lowered PM relative to certification diesel. The highest PM emissions were observed for methyl linolenate and a blend of methyl stearate and methyl linolenate. No consistent difference in emissions was observed between ethyl and methyl esters of the same feedstock. High peroxide value, acid number, and glycerine content had no effect on regulated pollutant emissions in this short-term study. These out-of-spec fuel properties may cause fouling in longer-term studies or in situations not investigated here.

The VOF emission for certification fuel (5.5% of 0.261 g/bhp-hr PM) is 0.0144 g/bhp-hr. For the biodiesels on average (21.4% of 0.07 g/bhp-hr), it is 0.0150 g/bhp-hr (results for biodiesels from real-world feedstocks). Neat biodiesel contains no sulfur and so sulfate emissions are significantly less for these fuels. Aldehyde emissions from various biodiesels are not significantly different than aldehyde emissions from certification diesel fuel.

The results indicate that PM reduction was proportional to oxygen content for biodiesels with a cetane number of greater than about 45 (density <0.89). Analysis indicated that NO_x emissions could be correlated by one parameter, either density or cetane number (which were highly correlated with each other). At the molecular structure level, NO_x emissions were correlated with increasing number of double bonds in the fatty acid chain. Highly saturated esters (with iodine number of 38 or less), exhibited NO_x emissions at or below the certification fuel level. Shortening of the fatty acid chain produced an increase in NO_x emissions, but NO_x was at or below the certification fuel level for methyl laurate (C12). The important conclusion is that fuel chemistry is at the root of all of these fuel properties and the increased NO_x emissions observed for many biodiesel fuels.

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Appendix A: Actual test sequence

Cert Fuel/Lot D-434	01/20/1999	3H
20% Methyl Soy/80% Cert	01/20/1999	3H
Cert Fuel/Lot D-434	01/21/1999	3H
20%LFFAG/80% Cert	01/21/1999	3H
Cert Fuel/Lot D-434	01/21/1999	2H
Soygold	01/22/1999	3H
Cert Fuel/Lot D-434	01/22/1999	2H
Methyl Linolenate	01/22/1999	2H
Cert Fuel/Lot D-434	01/25/1999	2H
Methyl Oleate	01/25/1999	2H
Cert Fuel/Lot D-434	01/26/1999	2H
Ethyl Oleate	01/26/1999	2H
Cert Fuel/Lot D-434	02/02/1999	H
Methyl Linoleate	02/02/1999	2H
Cert Fuel/Lot D-434	02/02/1999	2H
20%Inedible Tallow/80% Cert	02/04/1999	3H
Cert Fuel/Lot D-434	02/04/1999	3H
Cert Fuel/Lot D-434	02/26/1999	1C/3H
Methyl Laurate	02/26/1999	2H
Methyl Soy Ester IGT	03/01/1999	1C/3H
Cert Fuel/Lot D-434	03/01/1999	3H
Methyl Canola/Lot 9777	03/02/1999	1C/3H
Cert Fuel/Lot D-434	03/02/1999	2H
Methyl Lard/Lot 9811	03/03/1999	1C/3H
Cert Fuel/Lot D-434	03/03/1999	3H
Cert Fuel/Lot D-434	03/05/1999	3H
Cert Fuel/Lot D-434	03/08/1999	2H
Inedible Tallow Lot 10996	03/08/1999	3H
Cert Fuel/Lot D-434	03/08/1999	2H
Soygold	03/09/1999	1C/2H
Cert Fuel/Lot D-434	03/09/1999	2H
Edible Tallow Lot 112597	03/10/1999	1C/3H
Cert Fuel/Lot D-434	03/12/1999	6H
Methyl LFFA Grease Ester	03/15/1999	1C/3H
Cert Fuel/Lot D-434	03/15/1999	2H
Oxidized Methyl Soy Ester	03/16/1999	3H
Cert Fuel/Lot D-434	03/16/1999	2H
Ethyl Linoleate	03/16/1999	2H
Cert Fuel/Lot D-434	03/18/1999	3H
Ethyl Linseed	03/18/1999	2H
Cert Fuel/Lot D-434	03/19/1999	2H
2:1 MeStearate:MeLinseed	03/19/1999	2H
Cert Fuel/Lot D-434	03/19/1999	2H
Soygold	03/22/1999	1H
1:2 MeStearate:Me Linseed	03/22/1999	2H
Cert Fuel/Lot D-434	03/22/1999	2H
Ethyl Stearate	03/24/1999	2H

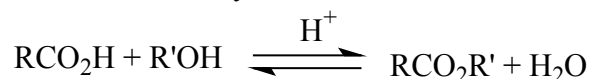
Cert Fuel/Lot D-434	03/24/1999	2H
Methyl Palmitate	03/24/1999	2H
Cert Fuel/Lot D-434	03/25/1999	2H
Ethyl Soy Ester	03/25/1999	2H
High AN Methyl Oleate	03/26/1999	2H
Cert Fuel/Lot D-434	03/26/1999	2H
Ethyl Hydrogenated Soy	03/26/1999	2H
Cert Fuel/Lot D-434	03/26/1999	2H
Ethyl Oxidized Soy Ester	03/29/1999	2H
Cert Fuel/Lot D-434	03/29/1999	2H
High Glyc Ethyl Soy Ester	03/30/1999	2H
Cert Fuel/Lot D-434	03/31/1999	4H
Methyl Stearate	03/31/1999	1H
Cert Fuel/Lot D-434	03/31/1999	2H
Methyl Hydrogenated Soy	04/02/1999	2H
Cert Fuel/Lot D-434	04/05/1999	3H
Cert Fuel/Lot D-434	04/27/1999	2H
Cert Fuel/Lot D-434	04/28/1999	2H
Soygold	04/28/1999	3H
Methyl HFFA Grease Ester	04/29/1999	3H
Cert Fuel/Lot D-434	04/29/1999	2H
Cert Fuel/Lot D-434	05/13/1999	2H
Cert Fuel/Lot D-434	02/18/2000	3H
Soygold	02/21/2000	3H
Methyl HFFA Grease Ester	02/22/2000	4H
Cert Fuel/Lot 9CP05201	02/25/2000	3H
Methyl HFFA Grease Ester	03/28/2000	2H
Methyl Soapstock Ester	03/28/2000	2H
Methyl Soapstock Ester, B-20	05/18/2000	2H
Cert Fuel/Lot D-434	05/18/2000	2H

Appendix B: Preparation of Esters

Purchased glassware list, all items duplicated unless noted.

Item	Manufacturer
3 Necked, 55/50 and 2* 24/40 22 L heavy wall RB flask	Corning
Custom distilling head	Allen Scientific Glassblowing
Condenser, long path 600 mm, 24/40	Corning, CIFER owned
Condenser, West, 600 mm, 24/40	Ace
1000 ml, pressure equalizing addition funnel	Ace
55/50 water cooled stirrer bearing	Ace
4' heavy duty stirrer shaft	Ace
Teflon stirrer blade	Ace
0-1000 rpm stirrer motor	Arrow
Stirrer motor chuck	Ace
24/40 stopper(total of 4)	Ace
55/50 stopper	Ace
22 L heating mantle	Ace
22 L heating mantle stand	Ace
Krytox [®] grease(total of 3 25 g tubes)	Dupont
Temperature controllers(total of 3), water switches, wiring and other supplies to build control box	Omega
Unistrut	Unistrut
5 gallon plastic and 8 gallon metal cans	
Miscellaneous supplies to build temporary laboratory structure and infra structure.	

Esterification of Free Acids. Acid catalyzed free esterification is shown in the following equation:



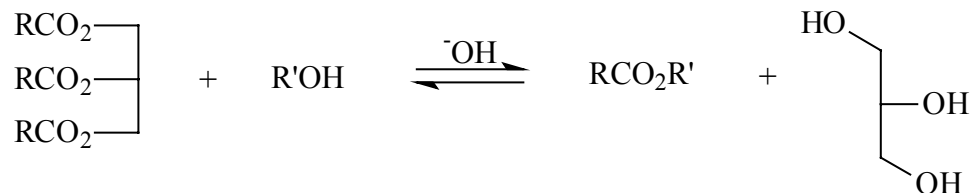
Methyl Oleate. Oleic Acid, technical grade (12 L, 37.8 Mol) and anhydrous methanol (4 L, 98.7 Mol) were stirred together and degassed under Ar_(g). Sulfuric acid (200 cm³, 3.7 Mol) was added over 10 minutes with a temperature gain of up to 10 °C. The mixture was stirred at reflux overnight and 75% of the excess methanol distilled. The mixture was cooled to room temperature, washed with distilled water (2 L) and then sodium bicarbonate solution (2 L). The crude methyl oleate typically had an acid number of 4.8 mg KOH g⁻¹. More water (2 L) and calcium hydroxide (100 g, 3.0 Mol) were added to the mixture, which was stirred slowly to effect reaction but not create an emulsion for 1 hour. The slurry was allowed to separate overnight, filtered and the product dried over sodium sulfate. The yield of methyl oleate was 63%, resulting in 8 L or 23.7 Mol of product, with an acid number of 0.2 mg KOH g⁻¹.

Ethyl Linoleate. Linoleic acid (12 L, 38.6 Mol) and ethanol (4 L, 68.9 Mol) were stirred together and degassed under Ar_(g). Sulfuric acid (200 cm³, 3.7 Mol) was added over 10 minutes with a temperature gain of up to 10 °C. The mixture was stirred at reflux overnight and the excess methanol distilled. The mixture was cooled to room temperature washed with distilled water (2 L) and then sodium bicarbonate solution (2 L). The crude ethyl linoleate had an acid number of *ca.* 5 mg KOH g⁻¹. The crude ethyl linoleate was dried over sodium sulfate, and twice distilled azeotropically with ethanol (4 L, 68.9 Mol) and

sulfuric acid (100 cm³). The ethyl linoleate yielded 12 L (36.5 Mol) of product or 94% conversion, with an acid number of 0.6 mgKOH g⁻¹.

These or similar procedures were also used to prepare methyl laurate, methyl palmitate, methyl and ethyl stearate, ethyl oleate, methyl linoleate, and high acid number methyl oleate.

Transesterification. The following reaction shows transesterification:

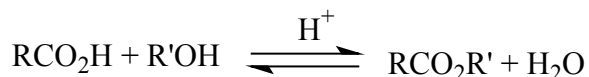


Methyl Linseed Ester. Linseed oil (12 L, 40.7 Mol) and methanol (4 L, 98.7 Mol) were stirred together and degassed under Ar_(g). Sodium hydroxide (100 g, 2.5 Mol) was then added and the mixture stirred at reflux overnight. With the heating turned off, sulfuric acid (200 cm³, 3.7 Mol) was added and 75% of the excess methanol distilled. The mixture was cooled to room temperature washed with water (4 x 2 L). The transesterification was repeated two additional times. Water (2 L) and calcium hydroxide (100 g, 3.0 Mol) were added to the mixture, which was stirred slowly to effect reaction but not create an emulsion for 1 hour. The slurry was allowed to separate overnight, filtered and the product dried over sodium sulfate. Methyl linseed ester was obtained as a dark brown oil (7 L, 20.6 Mol, 50%)

Ethyl Soy Ester. Methyl soy ester (12 L, 38.7 Mol) and ethanol (4 L, 68.9 Mol) were stirred together and degassed under Ar_(g). Sodium hydroxide (100 g, 2.5 Mol) was then added and the mixture stirred at reflux overnight. With the heating turned off, sulfuric acid (200 cm³, 3.7 Mol) was added and 75% of the excess ethanol distilled. The mixture was cooled to room temperature, washed with water (4 x 2 L) and dried, sodium sulfate. The crude ethyl soy ester was obtained as a dark yellow oil (12 L, 34.8 Mol, 90%), ethyl ester content 65%.

Other fuels prepared by transesterification were methyl and ethyl linseed, methyl and ethyl hydrogenated soy, ethyl oxidized soy, and high glyceride ethyl soy.

Discussion. All of these reactions are equilibrium reactions, catalyzed by either acid or base. In

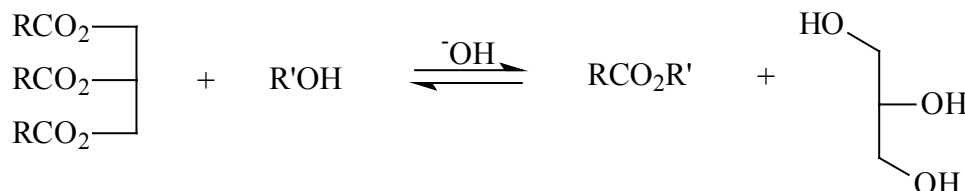


order to drive the reaction in the direction of the products, the equilibrium must be displaced by an excess of one or more reactants, or removal of one or more products. We were limited by the size of our reactors so that it was not practical to put in less starting oil than 12 L in order to maximize fuel throughput. In any case, equilibrium calculations revealed that ratios much larger than 2:1 did not result in larger displacement of the equilibrium for the acid catalyzed esterification of the acids. Sulfuric acid was used, as it is also a desiccant. The addition of sodium sulfate, a desiccant, resulted in no improvement of yield. This produced problems in meeting the biodiesel specifications for both acid number and glycerin content.

In the case of the esterification of the free acids, we wished to achieve a final acid number of <0.8 mg KOH g⁻¹, the biodiesel standard. An acid number of 0.8 mg KOH g⁻¹ represents an ester that is from 99.6% to 99.7% free of acid. It proved impossible to achieve better than a 97% conversion in one step, an acid number of 6 mg KOH g⁻¹, using a large excess of the alcohol. It was therefore necessary to remove the excess acid. There is a variety of methods available to remove the acid impurities, such as salt formation, distillation or membrane separation, but there was not enough time in the project to develop all

but the simplest methodology. The excess acid was reacted with commercial lime, calcium hydroxide, suspended in water to form the calcium salt of the acid. The calcium acid salts proved to be the most convenient metal acid salt to work with. Commercial lime can be obtained economically and the calcium salt forms an insoluble scum. The scum was removed by filtration from the resultant emulsion. Care had to be taken to agitate the mixtures enough to react all the excess acid, but not so much to form intractable emulsions. Removal of the excess acid was most effective for saturated acids at ambient temperature. It became harder to avoid intractable emulsion formation with an increasing in degrees of unsaturation. The fully saturated esters laurate and palmitate yielded 80% product, monounsaturated oleates yielded 75% product, diunsaturated linoleates yielded 50% product and triunsaturated linolenates yielded <50% product. To solve the problem of the low yield of ester from the doubly and triply unsaturated acids, the intractable emulsions were reacted with 10% sulfuric acid and the liming procedure repeated. A further problem was encountered for the esters with, melting points above ambient, the pure esters could not be filtered from these emulsions faster than the sparingly soluble basic calcium salts catalyzed hydrolysis back to the starting acids. The only way to obtain pure esters from the higher melting esters was by allowing the emulsions to stand for several days to separate; even so the yields were too low (25% or less) to be worthwhile.

For the ethyl case, we were able to reduce the acid number by taking advantage of azeotropic distillation. The ethanol distills as a 95% ethanol, 4% water azeotrope and so water is slowly removed from the reaction vessel pushing the equilibrium in the direction of the ethyl ester. This proved not to be an easy alternative, as the distillation had to be repeated three times. For the ethyl linoleate case, the acid number was 2.6 mg KOH g⁻¹ after one distillation, 1.4 mg KOH g⁻¹ after two distillations and 0.8 mg KOH g⁻¹, after three distillations. Because of the time constraints of the project, we were unable to perform this purification for all of the ethyl esters.



The biodiesel standard for free glycerol is <0.02 % and for bound glycerin <0.24%. The standard for free glycerol was easily met for all fuels as glycerol is soluble in water and all the fuels were washed with water. If the starting vegetable oil is 100% triglyceride then *ca.* 10% of it's weight will be bound glycerin. We found by experiment that repeated transesterification of linseed oil with a large excess of methanol gave bound glycerin values of 5.059%, or 50% conversion after 1 transesterification, 0.248% or 97% conversion, after 2 transesterifications and 0.039% or 99.6% conversion, after three transesterifications. It was therefore nessecary to transesterify all fuels starting from vegetable oils three time to obtain a product that met thebiodiesel specification. It proved very hard to keep the resultant fuels totally dry after each transesterification step and so the resultant acid number became unacceptably high, *ca.* 6 by the third transesterification. It was, therefore, nessecary to lime the transesterified fuels resulting in loss of product.

Because of this rather lengthy procedure to obtain fuels from vegetable oils we decided to try and synthesize the ethyl soy esters from commercial methyl soy ester in one step. We reasoned that as methanol is more volatile than ethanol, that the methanol could be distilled off before the ethanol, driving the reaction in the direction of the products. While better than the first transesterification step of the triglycerides (50% conversion), we only observed an enhancement to 65% conversion, and so these ethyl soy esters contained 35% methyl soy ester.

While GC-MS typically revealed less than 1% of products that could not be accounted for as identifiable fatty acid esters, the unsaturated fuels became appreciably darker on each pass through the reactor. We believe that this was most likely due to the charring action of the sulfuric acid catalyst and so this was added in smaller amounts for the more unsaturated acids and oils.

Appendix D: Fuel Analysis Results Reported by igt

<u>Test</u>	<u>LFFA</u> <u>Yellow</u> <u>Grease</u>	<u>HFFA</u> <u>Yellow</u> <u>Grease</u>	<u>Soy</u>	<u>Lard</u>	<u>Canola</u>	<u>Tallow</u>	<u>Inedible</u> <u>Tallow</u>
D86							
IBP, °F	624	594	613	580	600	616	611
10%, °F	633	623	643	612	615	634	631
20%, °F	635	627	649	616	628	637	634
50%, °F	640	632	654	624	636	646	639
90%, °F	655	647	669	638	645	665	658
EP, °F	665	667	673	670	671	682	675
Recovery, mL	99.5	99	98	98.5	99	98.2	99
Residue, mL	0.4	0.7	1.1	0.5	0.5	1.8	0.4
Loss, mL	0.1	0.3	0.7	1	0.5	0	0.6
D93 Flash, °F	320	297	333	263	326	344	276
D97 Pour, °F	48	43	25	55	25	60	59
D130 Corrosion	1A	1A	1A	1A	1A	1A	1A
D240 BTU, BTU/lb	17215	17154	17153	17165	17241	17144	17061
D445 Viscosity, cSt	5.62	4.66	4.546	4.85	4.63	4.908	4.93
D482 Ash, %	0.01	0.04	0	0	0.003	0.001	0
D524 Carbon Residue, %	0.04	0.05	0.01	0.04	0.04		0.08
D613 Cetane Number	52.2	53.2	59		53.9	64.8	54.3
D664 Acid Number, mg KOH/g	0.41	0.2	0.32	0.76	0.13	0.32	0.44
D971 Interfacial Tension			11.32	12.19	15.52	31.74	
D1094 Water rxn	N/A	N/A					N/A
D1160 Vacuum Distillation							
IBP, °F	650	616	658	629	658	628	606
5%, °F	664	650	662	648	662	646	642
10%, °F	664	653	663	650	663	648	648
20%, °F	667	656	665	652	663	652	653
30%, °F	667	659	666	653	663	656	655
40%, °F	670	660	667	655	664	660	659
50%, °F	670	660	669	659	664	662	662
60%, °F	672	663	670	661	664	666	665
70%, °F	674	665	671	664	666	669	667
80%, °F	678	668	674	669	668	674	670
90%, °F	687	673	687	672	672	680	678
95%, °F	720	681	849	679	685	689	695
EP, °F	902	832	883	768	814	793	895
Recovery, %	99	99	97	99	99	98	99
Residue + Loss, %	1	1	3	1	1	0.2	1
D1298 Specific Gravity	0.8789	0.8767	0.8877	0.8762	0.8811	0.8708	0.8767
D1322 Smoke Point	N/A	N/A	N/A	N/A	N/A	N/A	N/A
D1796 Sediment, %	0	0.03	0	0.6	0	0.05	0
D1959 Iodine, ppm	16.8	16.8	2.98	53	66	4.68	17.9
D2500 Cloud, °F	76	46	38	56	26	66	61
D2622 Sulfur, wt%	<DL	<DL	0	0	0	0	<DL

D2624 Conductivity	663	>9000	181	122	147	809	264
D3241 JFTOT							
Pressure drop	0	4	1	0	0	2	0
Tube rating	1	1	1	1	1	4P	1
D3242 Neutralization #, mg KOH/g	0.492	0.238	0.322	0.76	0.12	0.35	0.646
D4629 Total Nitrogen, ppm	4	48	3	3	0	77	5
D5191 Vapor pressure	N/A	N/A	N/A	N/A	N/A	N/A	N/A
D5291 Carbon/Hydrogen							
Carbon, wt%	76.2	76.03	77.95	77.36	77.68	77.07	75.88
Hydrogen, wt%	12.46	12.5	11.98	12.5	12.25	12.5	12.69
D6217 Particulate Matter, mg/L	N/A	0	2.56	789	11	74	1,154
C. Plank							
Free Glycerin	0	0.004	0.001	0	0.001	0	0
Monoglycerides, wt%	0.856	0.25	0.87	0.563	0.738	0.32	0.572
Diglycerides, wt%	0.233	0.076	1.358	0.093	0.02	0.12	0.07
Triglycerides, wt%	0	0	3.542	0.005	0.01	0.014	0
Total Glycerin, wt%	0.256	0.08	0.798	0.16	0.196	0.102	0.159
IP309 CFPP, °F	52	34	28	52	24	58	50

Appendix E: Analytical Results Supplied by ARS

Fatty Acid Speciation for Soapstock Methyl Ester

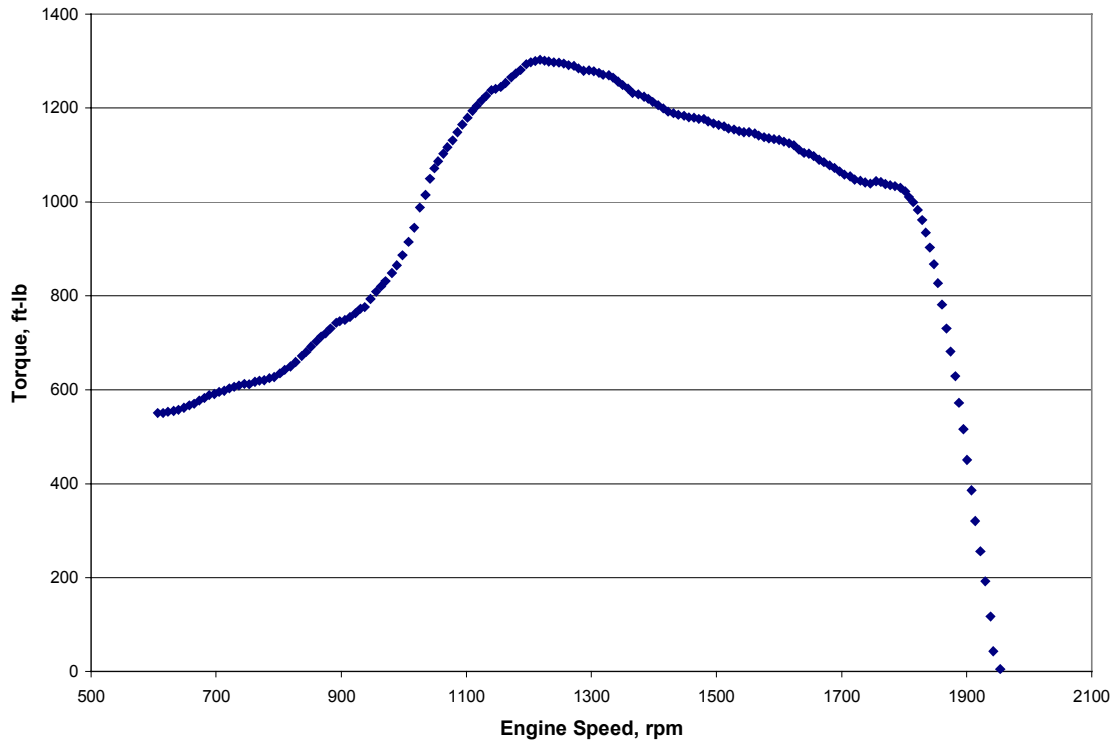
Fatty Acid Methyl Ester	Wt%
Stearic	16.1
Palmitic	4.7
Oleic	15.1
Possible 18:1, delta-11	1.2
Linoleic	54.4
Linolenic	6.9

Physical Property Data Measured by Williams Laboratory Services:

Flash Point:	169°C
Water and Sediment:	<0.01 vol. %
Carbon Residue, Ramsbottom:	0.01% Carbon Residue
Sulfated Ash:	0.020 mass %
Kinematic viscosity:	4.302 cSt @ 40°C
Sulfur:	0.0015 mass%
Cloud Point:	6°C
Copper Corrosion:	1A
Acid Number by Potentiometric Titration:	0.05 mg KOH/gram
Free Glycerin:	0.00 mass %
Monoglyceride:	0.448 mass %
Diglyceride:	0.025 mass %
Triglyceride:	0.031 mass %
Total Glycerin:	0.123 mass %

Appendix F: Engine Torque Map

The chart below shows the engine map, acquired on certification diesel fuel, that was used to generate the transient cycle for all transient runs in this test program (the map is run number 4421).



Appendix G: Emissions Data for Biodiesels from Various Sources

Engine emissions data for various biodiesels and for bracketing runs with certification fuel.

Run	Test Fuel		bhp-h	THC	NOx	CO	CO2	PM	VOF, % of	Fuel
				g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	PM	Economy
4422	Cert Fuel/Lot D-434	H	22.691	0.108	4.698	5.551	566.40	0.274	3.4%	7104
4426	Cert Fuel/Lot D-434	H	22.737	0.097	4.518	5.828	568.46	0.298	3.6%	7130
4427	Cert Fuel/Lot D-434	H	22.635	0.112	4.505	5.184	568.79	0.279	4.2%	7424
			Average	0.105	4.574	5.521	567.88	0.284	3.7%	
			CoV%	7.33%	2.37%	5.85%		4.39%	11%	
4428	20% Methyl Soy/80% Cert	H	22.659	0.111	4.655	4.892	568.61	0.221	5.7%	7454
4429	20% Methyl Soy/80% Cert	H	22.617	0.114	4.616	4.807	565.35	0.221	4.3%	7410
4430	20% Methyl Soy/80% Cert	H	22.656	0.114	4.610	4.864	567.26	0.221	2.8%	7435
			Average	0.113	4.627	4.854	567.07	0.221	4.3%	
			CoV%	1.21%	0.52%	0.90%		0.15%	33%	
4431	Cert Fuel/Lot D-434	H	22.642	0.114	4.663	5.870	568.43	0.290		7160
4432	Cert Fuel/Lot D-434	H	22.728	0.117	4.677	5.581	567.56	0.276		7108
			Average	0.116	4.670	5.725	568.00	0.283		
			CoV%	1.70%	0.21%	3.57%		3.53%		
4433	20%LFFAG/80% Cert	H	22.674	0.097	4.705	5.193	566.33	0.226	3.0%	7413
4434	20%LFFAG/80% Cert	H	22.714	0.088	4.702	5.133	565.68	0.224	3.4%	7403
4435	20%LFFAG/80% Cert	H	22.647	0.094	4.720	5.133	567.93	0.238	2.5%	7432
			Average	0.093	4.709	5.153	566.65	0.229	3.0%	
			CoV%	5.26%	0.22%	0.68%		3.32%	15%	
4437	Cert Fuel/Lot D-434	H	22.701	0.113	4.698	5.916	567.71	0.290		7035
4438	Cert Fuel/Lot D-434	H	22.688	0.105	4.736	5.570	568.90	0.280		7170
			Average	0.109	4.717	5.743	568.31	0.285		
			CoV%	4.73%	0.57%	4.27%		2.60%		

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
4443	Cert Fuel/Lot D-434	H	22.652	0.116	4.649	5.171	568.58	0.255		7370
4444	Cert Fuel/Lot D-434	H	22.690	0.110	4.702	5.229	567.43	0.266		7055
4449	Cert Fuel/Lot D-434	H	22.692	0.115	4.597	5.431	597.31	0.273		6908
4450	Cert Fuel/Lot D-434	H	22.708	0.101	4.613	5.208	568.22	0.244		--
4453	Cert Fuel/Lot D-434	H	22.593	0.095	4.636	5.744	562.37	0.294		6913
4454	Cert Fuel/Lot D-434	H	22.582	0.114	4.655	5.304	569.52	0.277		7195
4467	Cert Fuel/Lot D-434	H	22.434	0.097	4.538	5.752	573.55	0.301		7037
4472	Cert Fuel/Lot D-434	H	22.472	0.104	4.554	5.715	573.28	0.308		7121
4473	Cert Fuel/Lot D-434	H	22.447	0.102	4.544	5.649	573.77	0.296		7264
			Average	0.106	4.610	5.467	572.67	0.279		
			CoV%	7.54%	1.23%	4.54%		7.81%		
4475	20%Inedible Tallow/80% Cert	H	22.413	0.056	4.496	5.165	572.22	0.231		7140
4476	20%Inedible Tallow/80% Cert	H	22.454	0.074	4.526	4.978	614.82	0.239	1.8%	7737
4478	20%Inedible Tallow/80% Cert	H	22.428	0.076	4.508	4.816	572.16	0.238	2.2%	7364
			Average	0.069	4.510	4.986	586.40	0.236	2.0%	
			CoV%	16.03%	0.34%	3.50%		1.86%		
4479	Cert Fuel/Lot D-434	H	22.428	0.096	4.579	5.488	571.97	0.241		7080
4480	Cert Fuel/Lot D-434	H	22.413	0.101	4.549	5.164	571.62	0.279		7142
4481	Cert Fuel/Lot D-434	H	22.471	0.098	4.643	5.487	572.33	0.299		7289
			Average	0.098	4.590	5.380	571.97	0.273		
			CoV%	2.37%	1.05%	3.47%		10.67%		
4517	Cert Fuel/Lot D-434	C	22.399	0.135	5.080	6.860	617.10	0.340	4.1%	7747
4518	Cert Fuel/Lot D-434	H	22.476	0.132	4.588	5.194	573.24	0.301	4.4%	7130
4519	Cert Fuel/Lot D-434	H	22.646	0.124	4.666	5.806	570.45	0.311	4.9%	6995
4520	Cert Fuel/Lot D-434	H	22.565	0.123	4.637	5.530	571.13	0.315	12.3%	6963
			Composite	0.127	4.695	5.703	578.10	0.313	6.8%	
			Hot Average	0.126	4.630	5.510	571.60	0.309	7.2%	
			CoV%	4.11%	0.85%	5.56%		2.26%	61%	

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
4524	Methyl Soy Ester IGT	C	22.298	0.082	5.853	4.401	605.95	0.093	20%	7560
4525	Methyl Soy Ester IGT	H	22.301	0.078	5.246	3.243	573.80	0.078	20%	7279
4526	Methyl Soy Ester IGT	H	22.226	0.074	5.233	3.334	575.45	0.080	25%	7302
4527	Methyl Soy Ester IGT	H	22.307	0.074	5.225	3.503	576.47	0.085	19%	7318
			Composite	0.076	5.323	3.509	579.63	0.083	21%	
			Hot Average	0.075	5.234	3.360	575.24	0.081	21%	
			CoV%	3.26%	0.20%	3.93%		4.31%	14%	
4528	Cert Fuel/Lot D-434	H	22.427	0.110	4.679	4.983	574.55	0.243		7938
4529	Cert Fuel/Lot D-434	H	22.460	0.111	4.631	4.891	572.51	0.262		7341
4531	Cert Fuel/Lot D-434	H	22.459	0.110	4.632	4.985	574.10	0.264		7219
			Average	0.111	4.648	4.953	573.72	0.256		
			CoV%	0.72%	0.59%	1.09%		4.64%		
4532	Methyl Canola/Lot 9777	C	22.403	0.080	5.744	4.060	595.62	0.103	25%	7545
4533	Methyl Canola/Lot 9777	H	22.375	0.065	5.074	2.926	570.14	0.076	19%	7203
4534	Methyl Canola/Lot 9777	H	22.410	0.070	5.096	2.997	568.20	0.074	12%	7180
4535	Methyl Canola/Lot 9777	H	22.357	0.066	5.080	2.997	567.98	0.081	20%	6658
			Composite	0.069	5.178	3.129	572.61	0.081	18%	
			Hot Average	0.067	5.083	2.973	568.77	0.077	17%	
			CoV%	3.67%	0.22%	1.37%	0.00	4.75%	24%	
4536	Cert Fuel/Lot D-434	H	22.552	0.109	4.563	4.902	568.61	0.263		7466
4537	Cert Fuel/Lot D-434	H	22.541	0.069	4.582	4.719	570.20	0.260		7204
			Average	0.089	4.572	4.810	569.40	0.262		
			CoV%	31.89%	0.29%	2.68%		0.92%		
4539	Methyl Lard/Lot 9811	C	22.231	0.096	5.377	3.905	596.96	0.092	14%	7660
4540	Methyl Lard/Lot 9811	H	22.227	0.069	4.783	2.966	571.52	0.073	28%	7317
4541	Methyl Lard/Lot 9811	H	21.406	0.077	4.594	2.168	605.76	0.065	27%	7738
4542	Methyl Lard/Lot 9811	H	21.482	0.075	4.611	2.223	572.20	0.067	29%	7311
			Composite	0.077	4.765	2.660	585.13	0.072	26%	
			Hot Average	0.074	4.663	2.452	583.16	0.069	28%	
			CoV%	5.71%	2.24%	18.18%		6.07%	3%	

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
4545	Cert Fuel/Lot D-434	H	22.327	0.120	4.634	5.508	577.39	0.295		7398
4546	Cert Fuel/Lot D-434	H	22.299	0.112	4.604	4.902	569.94	0.277		7230
4547	Cert Fuel/Lot D-434	H	22.316	0.125	4.626	4.927	583.13	0.268		7131
4550	Cert Fuel/Lot D-434	H	22.435	0.131	4.632	5.135	568.86	0.259		7499
4551	Cert Fuel/Lot D-434	H	22.456	0.120	4.631	4.775	568.20	0.240		7734
4552	Cert Fuel/Lot D-434	H	22.466	0.116	4.626	4.718	568.08	0.221		7101
4553	Cert Fuel/Lot D-434	H	22.430	0.122	4.595	4.994	568.01	0.254		7094
4554	Cert Fuel/Lot D-434	H	22.474	0.120	4.603	4.926	566.67	0.253		7334
			Average	0.121	4.619	4.986	571.29	0.258		
			CoV%	4.53%	0.33%	4.94%		8.65%		
4555	Inedible Tallow Lot 10996	H	22.187	0.075	4.690	2.612	562.36	0.066	17%	7673
4556	Inedible Tallow Lot 10996	H	22.263	0.069	4.690	2.744	560.45	0.064	27%	7146
4557	Inedible Tallow Lot 10996	H	22.258	0.066	4.694	2.707	561.79	0.069	18%	7163
			Average	0.068	4.692	2.725	561.12	0.067	21%	
			CoV%	3.63%	0.07%	0.97%		4.53%	27%	
4560	Cert Fuel/Lot D-434	H	22.520	0.106	4.602	4.790	569.04	0.258		7068
4561	Cert Fuel/Lot D-434	H	22.538	0.104	4.579	4.630	566.84	0.243		7595
			Average	0.105	4.590	4.710	567.94	0.250		
			CoV%	1.25%	0.36%	2.40%		4.15%		
4566	Cert Fuel/Lot D-434	H	22.406	0.098	4.582	4.755	572.55	0.249		7913
4567	Cert Fuel/Lot D-434	H	22.349	0.106	4.578	4.606	568.30	0.248		7143
			Average	0.102	4.580	4.680	570.43	0.248		
			CoV%	5.25%	0.05%	2.25%		0.40%		
4569	Edible Tallow Lot 112597	C	22.039	0.055	5.105	3.697	590.32	0.076	26%	7577
4570	Edible Tallow Lot 112597	H	22.167	0.061	4.642	2.899	563.58	0.068	29%	7221
4571	Edible Tallow Lot 112597	H	22.204	0.061	4.648	2.866	561.08	0.071	26%	7189
4572	Edible Tallow Lot 112597	H	22.196	0.058	4.650	2.811	560.05	0.070	20%	7174
			Composite	0.059	4.712	2.978	565.68	0.071	25%	
			Hot Average	0.060	4.647	2.858	561.57	0.070	25%	
			CoV%	2.91%	0.08%	1.56%		2.23%	18%	

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
4574	Cert Fuel/Lot D-434	H	22.398	0.097	4.571	4.940	570.31	0.241		7177
4575	Cert Fuel/Lot D-434	H	22.406	0.107	4.569	4.580	568.36	0.232		7073
4576	Cert Fuel/Lot D-434	H	22.403	0.105	4.567	4.663	568.29	0.241		7126
4579	Cert Fuel/Lot D-434	H	22.416	0.106	4.612	5.238	570.66	0.274		7546
4583	Cert Fuel/Lot D-434	H	22.434	0.117	4.581	4.928	569.14	0.246		7715
4584	Cert Fuel/Lot D-434	H	22.450	0.097	4.581	4.836	567.45	0.247		7167
			Average	0.105	4.580	4.864	569.04	0.247		
			CoV%	7.09%	0.37%	4.78%		5.94%		
4585	Methyl LFFA Grease Ester	C	22.081	0.068	5.247	3.792	594.59	0.083	28%	7580
4586	Methyl LFFA Grease Ester	H	22.161	0.053	4.790	2.953	567.05	0.069	22%	7215
4587	Methyl LFFA Grease Ester	H	22.138	0.055	4.827	2.951	567.79	0.066	20%	7225
4588	Methyl LFFA Grease Ester	H	22.193	0.055	4.810	3.066	565.50	0.070	17%	7198
			Composite	0.056	4.871	3.104	570.76	0.070	21%	
			Hot Average	0.054	4.809	2.990	566.78	0.068	20%	
			CoV%	2.34%	0.38%	2.19%		3.52%	15%	
4589	Cert Fuel/Lot D-434	H	22.376	0.096	4.606	4.930	570.03	0.248		7769
4590	Cert Fuel/Lot D-434	H	22.383	0.094	4.601	4.693	570.59	0.237		7184
4594	Cert Fuel/Lot D-434	H	22.516	0.093	4.628	5.216	567.54	0.263		7184
4595	Cert Fuel/Lot D-434	H	22.526	0.093	4.654	4.993	565.78	0.263		7074
			Average	0.094	4.622	4.958	568.49	0.253		
			CoV%	1.50%	0.52%	4.34%		5.08%		
4674	Cert Fuel/Lot D-434	H	22.358	0.075	4.554	5.010	567.24	0.241		7881
4675	Cert Fuel/Lot D-434	H	22.373	0.079	4.545	4.794	565.97	0.242		6931
4676	Cert Fuel/Lot D-434	H	22.349	0.077	4.569	4.744	567.20	0.238		7163
4678	Cert Fuel/Lot D-434	H	22.242	0.067	4.481	4.726	561.95	0.253		7424
4679	Cert Fuel/Lot D-434	H	22.230	0.056	4.483	4.439	560.11	0.246		7269
4680	Cert Fuel/Lot D-434	H	22.267	0.044	4.466	4.763	563.22	0.259		7245
4681	Cert Fuel/Lot D-434	H	22.275	0.000	4.465	4.521	561.40	0.258		7202
			Hot Average	0.066	4.509	4.714	563.87	0.248		
			CoV%		1.00%	3.97%		3.42%		

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
4685	Methyl HFFA Grease Ester	H	21.783	*	4.719	2.508	558.69	0.058	16%	7204
4686	Methyl HFFA Grease Ester	H	21.818	*	4.744	2.406	557.21	0.057	12%	7004
4687	Methyl HFFA Grease Ester	H	21.758	*	4.737	2.405	558.31	0.058	18%	6903
			Hot Average		4.733	2.440	558.07	0.058	16%	
			CoV%		0.27%	2.41%		0.12%	17%	
4688	Cert Fuel/Lot D-434	H	22.234	*	4.480	4.206	561.34	0.216		7749
4690	Cert Fuel/Lot D-434	H	22.247	*	4.504	4.252	558.83	0.231		7482
			Hot Average		4.492	4.229	560.09	0.223		
			CoV%		0.38%	0.76%		4.98%		
Testing in February-March 2000:										
5201	Cert Fuel/Lot D-434	H	22.430	0.053	4.624	4.605	562	0.247	5.68%	7536
5202	Cert Fuel/Lot D-434	H	22.368	0.057	4.664	4.445	551	0.219	5.13%	6976
5203	Cert Fuel/Lot D-434	H	22.465	0.054	4.634	4.769	564	0.229	7.35%	7511
			Hot Average	0.055	4.640	4.606	559	0.232	6.1%	
			CoV%	3.29%	0.45%	3.51%	1.28%	6.03%	19.08%	
5204	Methyl Soyester (Soyagold)	H	22.106	0.034	5.054	2.967	564	0.078	18.29%	7503
5205	Methyl Soyester (Soyagold)	H	22.083	0.029	5.149	2.697	565	0.060	22.95%	7234
5206	Methyl Soyester (Soyagold)	H	22.056	0.031	5.153	2.577	564	0.060	21.31%	7167
			Hot Average	0.031	5.119	2.747	564	0.066	21%	
			CoV%	7.47%	1.10%	7.28%	0.08%	15.73%	11.33%	
5207	Methyl HFFA Grease Ester	H	21.951	0.019	4.917	2.589	564	0.054	29.09%	6794
5208	Methyl HFFA Grease Ester	H	21.957	0.030	5.025	2.492	567	0.057	32.20%	6895
5209	Methyl HFFA Grease Ester	H	21.914	0.027	4.769	2.472	565	0.054	35.71%	6847
5210	Methyl HFFA Grease Ester	H	21.900	0.028	4.974	2.409	566	0.056	31.03%	6825
			Hot Average	0.026	4.921	2.490	565	0.055	32%	
			CoV%	18.38%	2.26%	2.98%	0.25%	3.12%	8.69%	
5376	Soapstock Methyl Ester	H	21.329	0.018	5.035	2.370	581.137	0.096	22.77%	--
5377	Soapstock Methyl Ester	H	21.337	0.024	5.111	2.486	584.315	0.118	22.58%	--
			Hot Average	0.021	5.073	2.428	582.726	0.107		
			CoV%	21%	1%	3%	0%	14%		

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	VOF, % of PM	Fuel Economy btu/bhp-h
5494	Soapstock B20	H	22.522	0.043	4.698	4.608	570.495	0.192	10.14%	
5496	Soapstock B20	H	22.551	0.031	4.736	4.56	567.348	0.187	11.88%	
5497	Soapstock B20	H	22.553	0.029	4.712	4.416	569.565	0.173	14.29%	
			Hot Average	0.034	4.715	4.528	569.136	0.184		
			CoV%	22.05%	0.41%	2.21%	0.28%	5.35%		
5498	Cert Fuel/Lot D-434	H	22.645	0.04	4.673	4.67	565.429	0.221		
5499	Cert Fuel/Lot D-434	H	22.628	0.03	4.663	4.7	569.597	0.227		
			Hot Average	0.035	4.668	4.685	567.513	0.224		
			CoV%	20.20%	0.15%	0.45%	0.52%	1.89%		

Appendix H: Emissions Data for Pure Ester Biodiesels

Emissions testing results for biodiesels prepared from pure of nearly pure feedstocks.

Run	Test Fuel		bhp-h	THC	NOx	CO	CO2	PM	Fuel
				g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	Economy btu/bhp-h
4437	Cert Fuel/Lot D-434	H	22.701	0.113	4.698	5.916	567.707	0.290	7035
4438	Cert Fuel/Lot D-434	H	22.688	0.105	4.736	5.570	568.903	0.280	7170
			Average	0.109	4.717	5.743	568.305	0.285	
			CoV%	4.73%	0.57%	4.27%	0.15%	2.60%	
4440	Soygold	H	22.299	0.076	5.190	2.993	572.038	0.068	8454
4441	Soygold	H	22.299	0.067	5.233	2.909	570.387	0.063	8522
4442	Soygold	H	22.284	0.070	5.242	2.868	568.846	0.065	8396
			Average	0.071	5.222	2.924	570.423	0.065	
			CoV%	6.20%	0.53%	2.18%	0.28%	3.26%	
4443	Cert Fuel/Lot D-434	H	22.652	0.116	4.649	5.171	568.579	0.255	7370
4444	Cert Fuel/Lot D-434	H	22.690	0.110	4.702	5.229	567.429	0.266	7055
			Average	0.113	4.676	5.200	568.004	0.261	
			CoV%	3.71%	0.80%	0.79%	0.14%	2.85%	
4446	Methyl Linolenate	H	22.390	0.072	5.641	3.624	583.666	0.182	8060
4448	Methyl Linolenate	H	22.350	0.070	5.645	3.585	579.637	0.189	8074
			Average	0.071	5.643	3.605	581.652	0.186	
			CoV%	1.81%	0.06%	0.77%	0.49%	2.67%	
4449	Cert Fuel/Lot D-434	H	22.692	0.115	4.597	5.431	597.308	0.273	6908
4450	Cert Fuel/Lot D-434	H	22.708	0.101	4.613	5.208	568.222	0.244	0
			Average	0.108	4.605	5.319	582.765	0.258	
			CoV%	9.32%	0.25%	2.96%	3.53%	7.95%	
4451	Methyl Oleate	H	22.411	0.061	4.905	3.057	570.198	0.090	7945
4452	Methyl Oleate	H	22.389	0.053	4.918	3.144	570.987	0.086	0
			Average	0.057	4.912	3.101	570.593	0.088	
			CoV%	11.02%	0.18%	1.98%	0.10%	3.37%	
4453	Cert Fuel/Lot D-434	H	22.593	0.095	4.636	5.744	562.372	0.294	6913
4454	Cert Fuel/Lot D-434	H	22.582	0.114	4.655	5.304	569.521	0.277	7195
			Average	0.104	4.646	5.524	565.946	0.285	
			CoV%	12.71%	0.28%	5.64%	0.89%	4.32%	
4455	Ethyl Oleate	H	21.750	0.101	4.305	5.940	610.542	0.516	8340
4456	Ethyl Oleate	H	20.924	0.105	4.323	4.614	575.841	0.316	8270
			Average	0.103	4.314	5.277	593.191	0.416	
			CoV%	2.94%	0.29%	17.76%	4.14%	33.92%	

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	Fuel Economy btu/bhp-h
4467	Cert Fuel/Lot D-434	H	22.434	0.097	4.538	5.752	573.553	0.301	7037
4469	Methyl Linoleate	H	22.059	0.076	5.298	4.233	580.730	0.450	8164
4471	Methyl Linoleate	H	22.088	0.075	5.370	4.386	581.668	0.475	8086
			Average	0.076	5.334	4.309	581.199	0.463	
			CoV%	0.31%	0.96%	2.51%	0.11%	3.87%	
4517	Cert Fuel/Lot D-434	C	22.399	0.135	5.080	6.860	617.104	0.340	7747
4518	Cert Fuel/Lot D-434	H	22.476	0.132	4.588	5.194	573.239	0.301	7130
4519	Cert Fuel/Lot D-434	H	22.646	0.124	4.666	5.806	570.448	0.311	6995
4520	Cert Fuel/Lot D-434	H	22.565	0.123	4.637	5.530	571.128	0.315	6963
			Composite	0.127	4.695	5.703	578.105	0.313	
			Hot Average	0.126	4.630	5.510	571.605	0.309	
			CoV%	4.11%	0.85%	5.56%	0.25%	2.26%	
4521	Methyl Laurate	H	21.331	0.110	4.575	2.159	573.062	0.046	8252
4522	Methyl Laurate	H	21.347	0.101	4.570	1.987	573.615	0.043	6944
			Average	0.106	4.573	2.073	573.339	0.044	
			CoV%	6.18%	0.07%	5.87%	0.07%	4.41%	
4560	Cert Fuel/Lot D-434	H	22.520	0.106	4.602	4.790	569.042	0.258	7068
4561	Cert Fuel/Lot D-434	H	22.538	0.104	4.579	4.630	566.836	0.243	7595
			Average	0.105	4.590	4.710	567.939	0.250	
			CoV%	1.25%	0.36%	2.40%	0.27%	4.15%	
4562	Soygold	C	22.258	0.095	5.851	4.146	598.194	0.096	8499
4563	Soygold	H	22.306	0.069	5.292	3.146	572.256	0.074	8107
4564	Soygold	H	22.270	0.068	5.198	2.993	567.349	0.072	8012
			Composite	0.072	5.331	3.223	573.858	0.076	
			Hot Average	0.068	5.245	3.070	569.803	0.073	
			CoV%	1.45%	1.27%	3.52%	0.61%	1.80%	
4566	Cert Fuel/Lot D-434	H	22.406	0.098	4.582	4.755	572.555	0.249	7913
4567	Cert Fuel/Lot D-434	H	22.349	0.106	4.578	4.606	568.303	0.248	7143
			Average	0.102	4.580	4.680	570.429	0.248	
			CoV%	5.25%	0.05%	2.25%	0.53%	0.40%	
4589	Cert Fuel/Lot D-434	H	22.376	0.096	4.606	4.930	570.031	0.248	7769
4590	Cert Fuel/Lot D-434	H	22.383	0.094	4.601	4.693	570.591	0.237	7184
			Hot Average	0.095	4.604	4.812	570.311	0.242	
			CoV%	1.36%	0.08%	3.49%	0.07%	3.07%	

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	Fuel Economy btu/bhp-h
4591	Oxidized Methyl Soy Ester	H	22.204	0.072	5.199	2.821	570.318	0.066	8128
4592	Oxidized Methyl Soy Ester	H	22.270	0.055	5.199	2.825	569.273	0.069	7987
4593	Oxidized Methyl Soy Ester	H	22.229	0.051	5.205	2.797	568.999	0.068	7843
			Hot Average	0.059	5.201	2.814	569.530	0.068	
			CoV%	18.71%	0.06%	0.54%	0.12%	1.92%	
4594	Cert Fuel/Lot D-434	H	22.516	0.093	4.628	5.216	567.544	0.263	7184
4595	Cert Fuel/Lot D-434	H	22.526	0.093	4.654	4.993	565.780	0.263	7074
			Hot Average	0.093	4.641	5.104	566.662	0.263	
			CoV%	0.04%	0.39%	3.09%	0.22%	0.01%	
4596	Ethyl Linoleate	H	22.143	0.058	5.370	3.243	575.815	0.076	8417
4597	Ethyl Linoleate	H	22.143	0.057	5.353	3.231	576.329	0.073	6577
			Hot Average	0.057	5.361	3.237	576.072	0.075	
			CoV%	1.30%	0.23%	0.27%	0.06%	2.80%	
4599	Cert Fuel/Lot D-434	H	22.697	0.000	4.574	5.106	561.018	0.246	6325
4600	Cert Fuel/Lot D-434	H	22.753	0.085	4.604	4.914	564.921	0.262	6373
4602	Cert Fuel/Lot D-434	H	22.767	0.086	4.604	5.305	567.882	0.250	6413
			Hot Average	0.086	4.594	5.108	564.607	0.252	
			CoV%	0.40%	0.38%	3.83%	0.61%	3.37%	
4603	Ethyl Linseed	H	22.350	0.081	5.322	3.709	582.845	0.144	6551
4604	Ethyl Linseed	H	22.481	0.000	4.966	3.896	516.134	0.129	5805
			Hot Average	0.040	5.144	3.802	549.490	0.137	
			CoV%	141.42%	4.90%	3.47%	8.58%	7.82%	
4605	Cert Fuel/Lot D-434	H	22.684	0.103	4.632	5.215	571.168	0.248	6448
4606	Cert Fuel/Lot D-434	H	22.757	0.101	4.669	5.303	570.578	0.268	6443
			Hot Average	0.102	4.650	5.259	570.873	0.258	
			CoV%	1.60%	0.57%	1.19%	0.07%	5.49%	
4607	2:1 MeStearate:MeLinseed	H	15.780	0.846	4.571	8.490	596.000	1.890	7457
4609	2:1 MeStearate:MeLinseed	H	6.946	0.980	7.239	10.941	711.861	1.366	7214
4612	Cert Fuel/Lot D-434	H	22.313	0.116	4.487	4.933	579.261	0.284	6863
4613	Cert Fuel/Lot D-434	H	22.396	0.097	4.485	4.776	571.140	0.272	8094
			Hot Average	0.106	4.486	4.855	575.200	0.278	
			CoV%	12.68%	0.03%	2.29%	1.00%	3.25%	
4614	Soygold	H	21.745	0.082	5.046	2.826	572.920	0.071	8132

Run	Test Fuel		bhp-h	g/bhp-h	THC	NOx	CO	CO2	PM	Fuel Economy
					g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	btu/bhp-h
4615	1:2 MeStearate:Me Linseed	H	21.814	0.071	4.831	3.307	581.020	0.156		7283
4616	1:2 MeStearate:Me Linseed	H	21.031	0.086	4.728	2.990	587.457	0.197		8132
			Hot Average	0.079	4.779	3.149	584.239	0.176		
			CoV%	14.06%	1.51%	7.12%	0.78%	16.52%		
4617	Cert Fuel/Lot D-434	H	22.336	0.110	4.512	4.830	571.672	0.256		7283
4618	Cert Fuel/Lot D-434	H	22.422	0.100	4.543	4.895	570.444	0.268		7106
			Hot Average	0.105	4.528	4.862	571.058	0.262		
			CoV%	7.29%	0.49%	0.94%	0.15%	3.38%		
4620	Ethyl Stearate	H	21.745	0.073	4.328	2.397	557.331	0.059		7958
4621	Ethyl Stearate	H	21.841	0.085	4.294	2.352	590.821	0.068		7915
			Hot Average	0.079	4.311	2.374	574.076	0.064		
			CoV%	10.87%	0.56%	1.33%	4.13%	10.18%		
4622	Cert Fuel/Lot D-434	H	22.493	0.091	4.519	5.035	571.047	0.269		7224
4623	Cert Fuel/Lot D-434	H	22.463	0.091	4.522	4.781	570.016	0.257		7069
			Hot Average	0.091	4.520	4.908	570.531	0.263		
			CoV%	0.42%	0.05%	3.65%	0.13%	3.08%		
4626	Methyl Palmitate	H	21.708	0.048	4.328	2.183	564.444	0.064		8552
4627	Methyl Palmitate	H	21.762	0.045	4.294	2.189	561.860	0.057		0
			Hot Average	0.046	4.311	2.186	563.152	0.060		
			CoV%	4.65%	0.56%	0.18%	0.32%	7.70%		
4630	Cert Fuel/Lot D-434	H	22.510	0.094	4.526	4.941	571.454	0.243		7120
4631	Cert Fuel/Lot D-434	H	22.530	0.096	4.586	4.689	570.869	0.259		7171
			Hot Average	0.095	4.556	4.815	571.162	0.251		
			CoV%	2.08%	0.92%	3.70%	0.07%	4.62%		
4632	Ethyl Soy Ester	H	22.056	0.094	5.206	3.004	620.367	0.083		8224
4633	Ethyl Soy Ester	H	21.901	0.098	5.111	2.741	572.025	0.069		7961
			Hot Average	0.096	5.158	2.872	596.196	0.076		
			CoV%	3.42%	1.31%	6.49%	5.73%	13.75%		
4636	High AN Methyl Oleate	H	21.863	0.041	4.861	2.634	573.162	0.068		8144
4638	High AN Methyl Oleate	H	21.846	0.052	4.827	3.085	574.243	0.085		8031
			Hot Average	0.046	4.844	2.859	573.703	0.076		
			CoV%	17.01%	0.49%	11.16%	0.13%	15.81%		

Run	Test Fuel		bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	g/bhp-h	Fuel Economy btu/bhp-h
				THC	NOx	CO	CO2	PM	
4640	Cert Fuel/Lot D-434	H	22.370	0.083	4.519	5.110	565.865	0.273	0
4641	Cert Fuel/Lot D-434	H	22.361	0.080	4.530	5.080	572.394	0.276	7383
			Hot Average	0.082	4.524	5.095	569.130	0.275	
			CoV%	2.74%	0.17%	0.42%	0.81%	0.82%	
4642	Ethyl Hydrogenated Soy	H	21.695	0.049	4.342	2.540	565.443	0.074	7814
4643	Ethyl Hydrogenated Soy	H	21.761	0.004	4.285	2.738	563.788	0.078	7859
			Hot Average	0.027	4.314	2.639	564.616	0.076	
			CoV%	119.79%	0.94%	5.31%	0.21%	3.61%	
4644	Cert Fuel/Lot D-434	H	22.313	0.088	4.554	5.007	570.123	0.265	7506
4645	Cert Fuel/Lot D-434	H	22.335	0.082	4.580	5.241	570.905	0.283	7176
			Hot Average	0.085	4.567	5.124	570.514	0.274	
			CoV%	4.75%	0.39%	3.23%	0.10%	4.66%	
4647	Ethyl Oxidized Soy Ester	H	22.128	0.047	5.105	2.851	573.654	0.069	7779
4648	Ethyl Oxidized Soy Ester	H	21.976	0.050	5.098	2.591	572.162	0.066	8068
			Hot Average	0.048	5.101	2.721	572.908	0.067	
			CoV%	3.42%	0.09%	6.76%	0.18%	3.55%	
4649	Cert Fuel/Lot D-434	H	22.373	0.116	4.572	4.777	569.562	0.237	7296
4650	Cert Fuel/Lot D-434	H	22.371	0.076	4.552	4.583	569.505	0.250	7122
			Hot Average	0.096	4.562	4.680	569.534	0.244	
			CoV%	29.17%	0.30%	2.92%	0.01%	3.54%	
4651	High Glyc Ethyl Soy Ester	H	21.887	0.056	5.024	2.995	576.585	0.074	8025
4652	High Glyc Ethyl Soy Ester	H	21.894	0.050	5.034	3.079	575.354	0.079	7963
			Hot Average	0.053	5.029	3.037	575.970	0.076	
			CoV%	8.39%	0.13%	1.96%	0.15%	4.77%	
4653	Cert Fuel/Lot D-434	H	22.271	0.082	4.606	4.931	573.233	0.243	7138
4654	Cert Fuel/Lot D-434	H	22.268	0.083	4.580	4.836	572.276	0.254	7205
4657	Cert Fuel/Lot D-434	H	22.278	0.081	4.573	5.106	570.172	0.271	7027
4660	Cert Fuel/Lot D-434	H	22.277	0.079	4.593	5.428	572.056	0.283	7028
			Hot Average	0.081	4.588	5.075	571.934	0.263	
			CoV%	2.27%	0.32%	5.13%	0.22%	6.72%	
4664	Methyl Stearate	H	21.515	0.038	4.236	3.499	568.424	0.149	0

Run	Test Fuel		bhp-h	THC g/bhp-h	NOx g/bhp-h	CO g/bhp-h	CO2 g/bhp-h	PM g/bhp-h	Fuel Economy btu/bhp-h
4665	Cert Fuel/Lot D-434	H	22.209	0.081	4.616	5.144	570.946	0.274	7241
4666	Cert Fuel/Lot D-434	H	22.233	0.080	4.601	5.025	570.187	0.272	7042
			Hot Average	0.081	4.608	5.085	570.566	0.273	
			CoV%	0.81%	0.23%	1.66%	0.09%	0.63%	
4672	Methyl Hydrogenated Soy	H	21.741	0.043	4.285	2.692	563.050	0.072	7925
4673	Methyl Hydrogenated Soy	H	16.263	0.074	4.254	2.273	590.376	0.078	0
			Hot Average	0.058	4.269	2.482	576.713	0.075	
			CoV%	37.62%	0.52%	11.93%	3.35%	5.93%	
4674	Cert Fuel/Lot D-434	H	22.358	0.075	4.554	5.010	567.238	0.241	7881
4675	Cert Fuel/Lot D-434	H	22.373	0.079	4.545	4.794	565.971	0.242	6931
4676	Cert Fuel/Lot D-434	H	22.349	0.077	4.569	4.744	567.202	0.238	7163
4678	Cert Fuel/Lot D-434	H	22.242	0.067	4.481	4.726	561.947	0.253	7424
4679	Cert Fuel/Lot D-434	H	22.230	0.056	4.483	4.439	560.110	0.246	7269
4680	Cert Fuel/Lot D-434	H	22.267	0.044	4.466	4.763	563.219	0.259	7245
4681	Cert Fuel/Lot D-434	H	22.275	0.000	4.465	4.521	561.397	0.258	7202
			Hot Average	0.066	4.509	4.714	563.869	0.248	
			CoV%	20.78%	1.00%	3.97%	0.52%	3.42%	

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