

**EFFECT OF BIODIESEL COMPOSITION ON NO_x AND PM EMISSIONS FROM A
DDC SERIES 60 ENGINE**

DRAFT
FINAL REPORT

to

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SUMMARY

The National Renewable Energy Laboratory is conducting an investigation of various biodiesel fuels produced from waste oils. As an important part of this study, data on emissions based on the EPA heavy-duty transient cycle have been measured to demonstrate the sensitivity of engine emissions to biodiesel ester composition. 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 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, 27 neat biodiesels and 3 B-20 blends (with EPA certification diesel) were tested. Seven fuels prepared from various natural feedstocks were obtained from IGT, and three of these were also tested as B-20 blends. Twenty fuels were prepared at the Colorado School of Mines, 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 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 also measured for many of the fuels. Samples for PAH and biological activity analysis by the University of California at Davis were collected.

All fuels tested 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. 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 (+/-0.3%) with no significant drift over the 4 month test program. PM emissions averaged 0.261 g/bhp-h (+/-2.7%). 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 correction was applied to the PM data.

Testing of the biodiesels produced from natural sources (supplied by IGT) indicated that PM emissions 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 and soy) produced the highest NO_x emissions. 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 methyl palmitate, methyl laurate, ethyl 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 in longer term studies, or storage and handling problems.

Regression analysis of the results indicated that emissions could be correlated by one parameter, either density or cetane number (which were highly correlated with each other). 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 biodiesel density or cetane number. These results suggest that neat biodiesels with cetane numbers greater than about 60 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 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 the NO_x emission is also 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 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 is conducting an investigation of various biodiesel fuels produced from waste oils. As an important part of this study, data on emissions based on the EPA heavy-duty transient cycle are necessary to demonstrate the possible sensitivity of engine emissions to biodiesel ester composition. Here 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 on 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 CO up to 50%. Oxygenates are now mandated under the Clean Air Act for use in reformulated and CO control gasoline. This 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 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, CO was 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%. The data suggest 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, although several significant studies have not. 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 (oxygenates contain 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.

Parker (1996) has recently speculated on other possible causes for increased NO_x during soyester combustion:

1. An increase in the flame temperature in either the premixed or diffusional burn regimes. While oxygenated fuels have a lower adiabatic flame temperature, carbonaceous PM or soot particles are very effective heat radiators. Therefore, the net result of the PM reduction caused by supplying oxygen to the fuel pyrolysis zone may be to increase flame temperature because of this loss of radiant heat transfer.
2. Spray properties may be altered due to differences in viscosity, surface tension, and fuel boiling point for the oxygenated fuels. Spray properties affected may include droplet size, droplet momentum and hence degree of mixing and penetration, evaporation rate, and radiant heat transfer rate. A change in any of these properties might lead to different relative duration of the premixed versus diffusional burn regimes. Since it is possible that different fuel fractions are consumed in premixed and diffusional burn, and since the two burning processes may have different pollutant formation characteristics, this difference in ignition delay could be the cause of the increased NO_x emission. Changes in spray properties may also change characteristics of the diffusional burn regime that lead to increased flame temperature and higher levels of NO_x formation.
3. Ignition delay within an engine can be a function of both the fuel used and fuel spray properties (Sato, et al., 1986). The importance of ignition delay is that longer delays provide time for more fuel to become "premixed" and therefore to be consumed in the premixed phase rather than in the diffusional burn phase with possible differences in emissions as discussed above.
4. Fuel chemistry effects in the flame region could account for a change in nitric oxide production. Thermal, or "Zeldovich" NO is unaffected by fuel chemistry; however, prompt NO can account for 30% or more of the total nitric oxide emission (Miller and Bowman, 1989). Since prompt nitric oxide is sensitive to radical concentrations at the flame front, an increase in prompt NO could be attributed to fuel chemistry effects.

Removal of the carbonaceous PM from the combustion environment may eliminate NO-carbon reactions. The importance of NO-carbon reactions in diesel combustion is unknown.

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 strong evidence that higher boiling oxygenates such as 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. In the current investigation 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. All neat fuels were tested and three were tested as B-20 blends. The second set of fuels was prepared by CIFER from pure, or nearly pure, fatty acids and from several feedstock fats. 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 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 available 50 gallons of highly oxidized (peroxide value of about 2000) methyl soy ester stored in our lab, and utilized this material instead. Ethyl esters were prepared by transesterification 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 |
|------------------------------------|
| <i>Supplied by IGT</i> |
| 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 |
| <i>Prepared at CSM</i> |
| 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:

All fuels tested were prepared according to the NBB Specification shown in Table 3. In a number of circumstances, it was not possible to meet the specification as it was developed for soy diesel. The effect of certain properties not meeting the specification is discussed in the emissions testing section.

Table 3. Biodiesel Specification for Pure (100%) Biodiesel (12/6/96).

| 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 % |

¹ Christina Planc procedure

Fuel Preparation:

Apparatus: Two identical reactors were built. Each reactor consisted of a 22 L round bottom heavy walled three necked flask surrounded by and supported in a heating mantle which was located in a floor cradle. The central larger bore, 55/50, neck contained the water cooled stirrer bearing which in turn supported a 4' foot heavy duty stirrer shaft which propelled a Teflon stirrer blade and was driven by a high torque, 0-1000 rpm laboratory stirrer. 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 dry argon was introduced to the system through the uppermost reactor after initial purging of the system. 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 no material escaped from this. 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 below. All fuels were stored

under argon in cans containing muslin bags of desiccant, sodium sulfate. The methanol used in these reactions was recycled after drying. Examples of synthesis methods are given in Appendix B.

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. 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, which enables us to speciate the impurities, and a 0.2 uL injection, which gives us a nice peak shape 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 Balances: 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 through weighing of 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. Fuel 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 53F nominal dew point to insure that the NO_x correction factor (40CFR 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 which 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. 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. Particle filter handling and weighing is conducted in a yellow light, constant humidity weigh room held at $9\pm 2^{\circ}\text{C}$ ($48\pm 4^{\circ}\text{F}$) dew point, 50% nominal relative humidity and $22\pm 1^{\circ}\text{C}$ ($72\pm 2^{\circ}\text{F}$).

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 weight 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 three proportional, diluted exhaust samples in accordance with the Code of Federal Regulations (CFR 40 Part 86 Subpart N) is employed. Each 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. These sampling systems can be fitted with filters for PM sampling or with DNPH sorbents for aldehyde sampling. 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 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 and PAH 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 the sampling system 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 provided by IGT

In this program, IGT provided six feedstocks made from non-soy fats plus a soydiesel. IGT also provided some analytical data for these materials. 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.

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 (see end of this section) shows properties measured for fuels prepared under this project. The methyl soy ester was donated by AG Environmental products. 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 on purpose 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 exceeded 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. To determine if oxidation produced instantaneous emissions effects, two soy fuels were contacted with air and the peroxide numbers of the fuels were raised considerably. These fuels were emissions tested.

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 preparation of ethyl soy and oxidized ethyl soy esters by transesterification of methyl esters.

The original plan was to produce very pure esters so that 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- <i>Linseed for blending</i> | 0.4 | -- | -- | 0/0.132 | -- | -- | -- | -- | -- | -- |
| M- <i>Linseed/M-Stearate 2:1</i> | 1.62 | 116 | 295 | 0/0.032 | 0 | -- | -- | -- | -- | -- |
| M- <i>Linseed/M-Stearate 1:2</i> | 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- <i>Linseed</i> | 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 M | C14:0 M | C14:1M | C16:0 M | C16:0 E | C16:1 M | C17:0 M | C18:0 M | C18:0 E | C18:1 M | C18:1 E | C18:2 M | C18:2 E | C18:3 M |
|--------------------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|---------|
| MW | 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 |
| Unsat | 0 | 0 | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 1 | 1 | 2 | 2 | 3 |
| E-Hydrogenated Soy | 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.

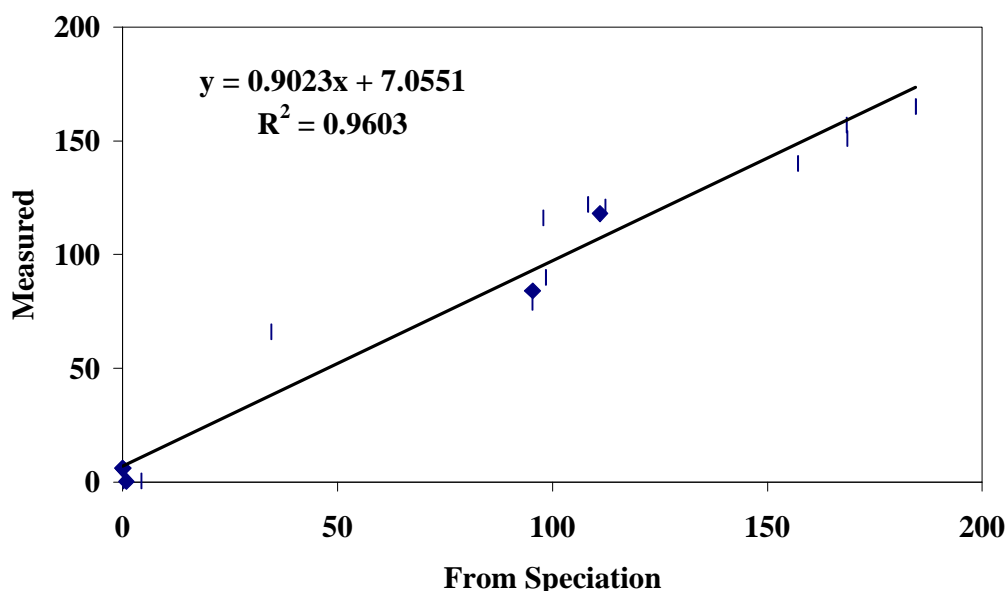


Figure 1 Comparison of measured iodine number with value calculated from fatty acid speciation data.

Density and Energy Density:

Since the 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. Heating values for the IGT fuels as reported by us (CIFER) and IGT are compared 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 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 and it is concluded that the heating value is constant. Thus, we conclude that heating values of the fuels produced here are consistent with those reported by

previous researchers and that the energy density per volume injected is directly proportional to the fuel density.

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 | 0 | |
| Mean Difference | | |
| 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 | 17334 |

¹ Ethyl tallow not included.

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.

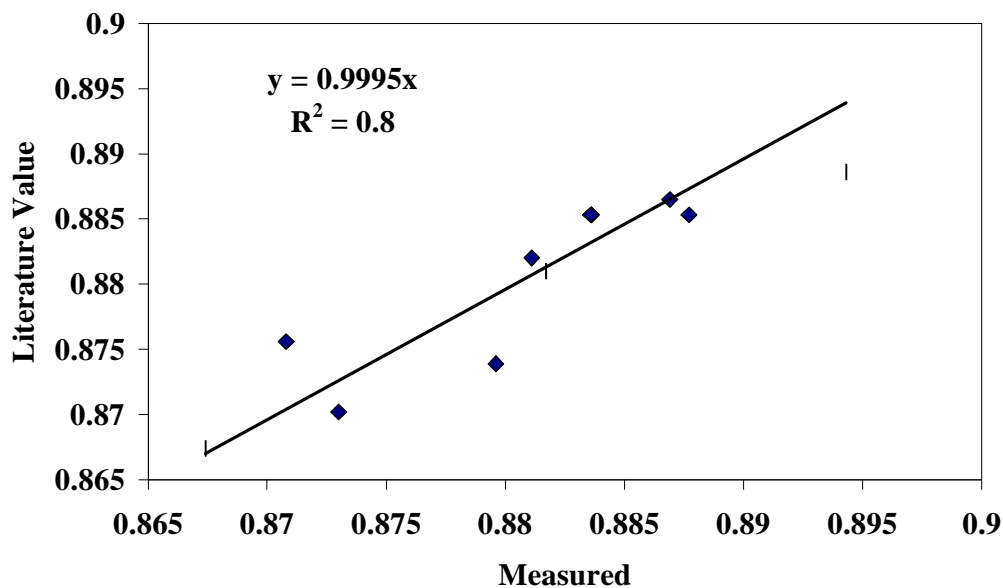


Figure 2. Parity Plot for Measured Versus Reported Density

Cetane Number:

The Cetane Number is a gross measure of ignition delay for fuel combustion. Figure 3 presents a parity plot for literature¹ and measured Cetane Number values. The agreement is excellent except for methyl linolenate (22.7 versus 45.9 measured in this study). The literature Cetane Number is much lower than the Cetane Number observed for the fuel manufactured in this program. The ASTM D-976 test does not replicate Cetane Numbers 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 Numbers reported in the literature by Graboski and McCormick, the literature value may be more correct for methyl linolenate.

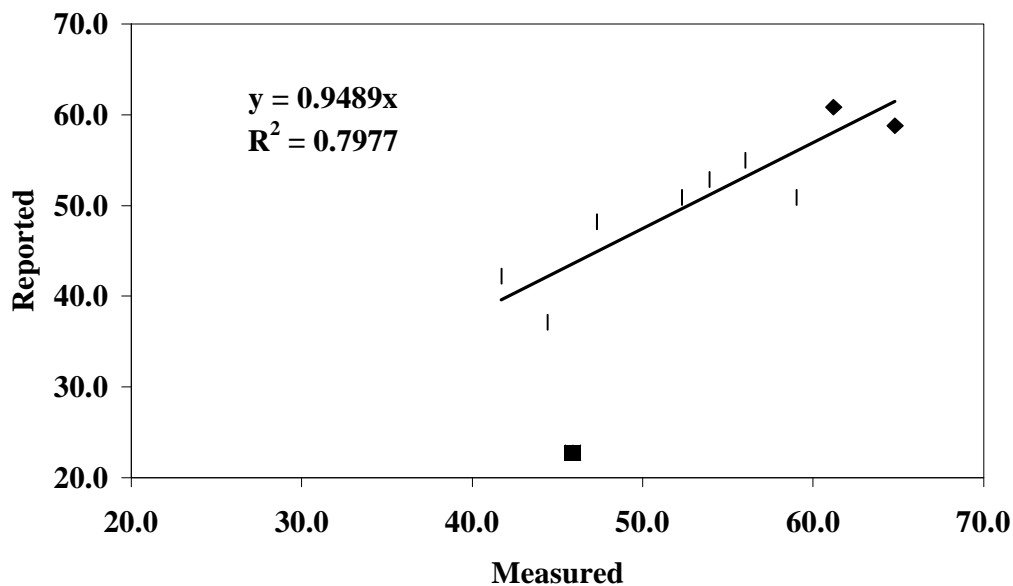


Figure 3. Parity Plot for Measured Versus Reported Cetane Number.

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 40C. 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.

| 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 all subsequent testing on all fuels. A plot of the torque map is shown in Appendix E. 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.

Tables 12 and 13 present descriptive statistics for the certification fuel runs. The 95% confidence limits for NO_x and PM are +/- 0.3% and +/- 2.7% respectively. The median and mean are very close suggesting that the majority of the variance is due to random fluctuations in the data and not a large time series effect.

Table 12. Descriptive Statistics for NO_x Emissions from a 1991 DDC Series 60 Engine using EPA Certification Diesel.

| | |
|--------------------------|---------|
| Mean | 4.59430 |
| Standard Error | 0.00629 |
| Median | 4.58700 |
| Standard Deviation | 0.05334 |
| Sample Variance | 0.00285 |
| Range | 0.25122 |
| Minimum | 4.48526 |
| Maximum | 4.73648 |
| Count | 72 |
| Confidence Level (95.0%) | 0.01254 |

Table 13. 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 |

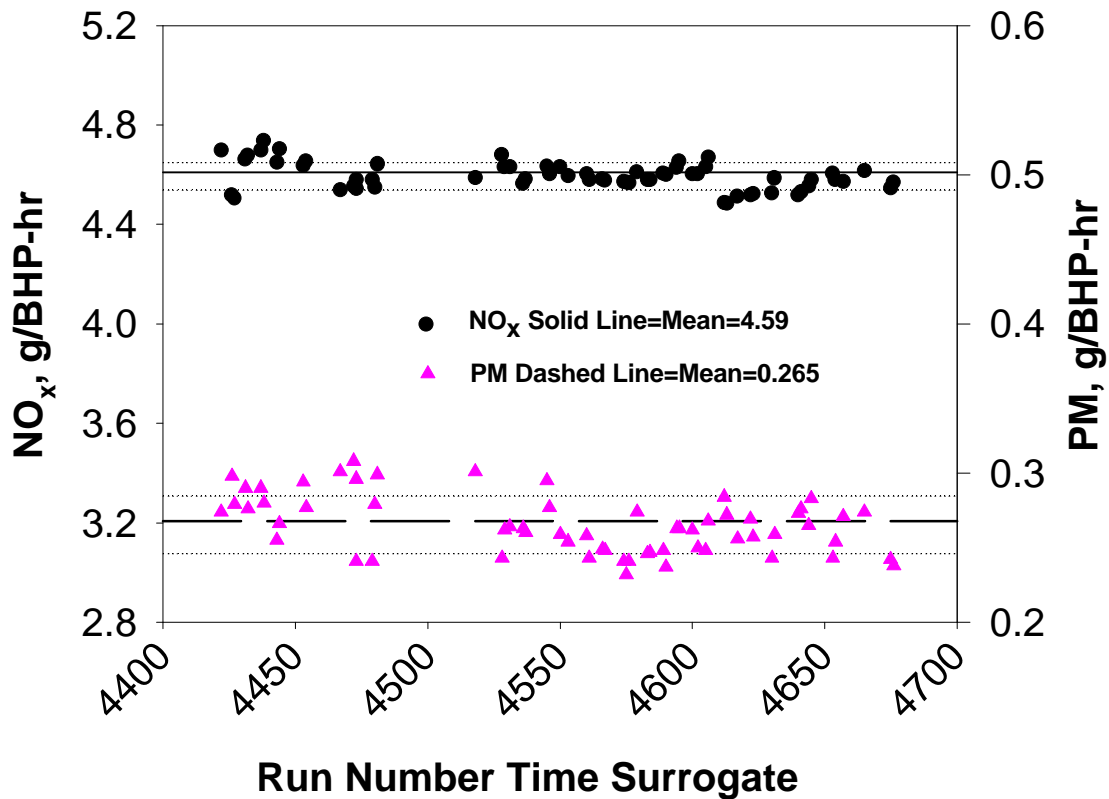


Figure 4. NO_x and PM emissions results for certification fuel runs performed over the study.

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.

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 reference 3, 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 a 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.

Table 14. 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. 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 | |

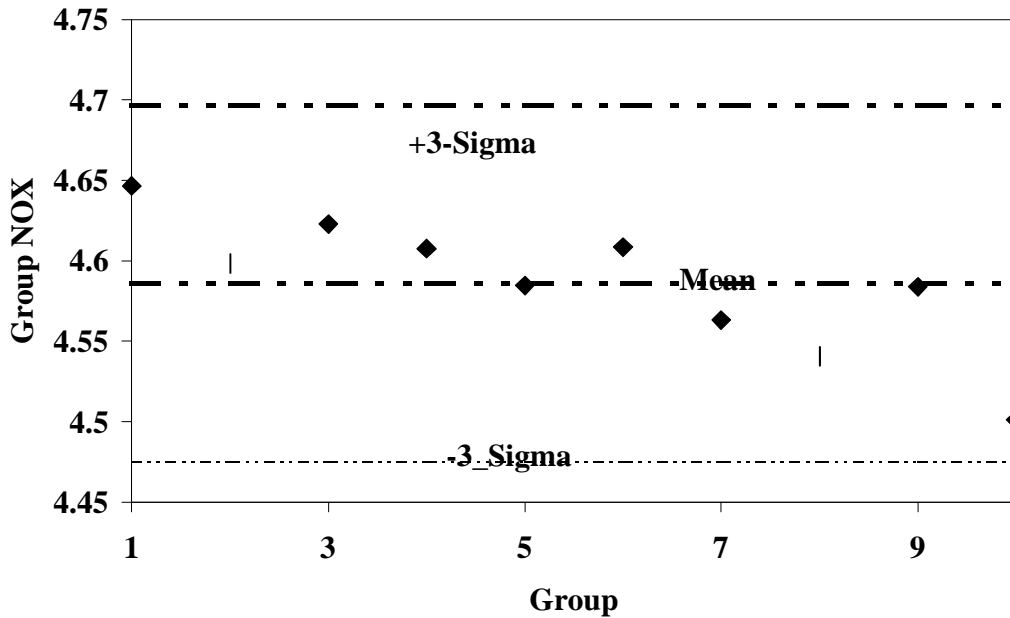


Figure 5. Shewhart means control plot for certification fuel NO_x emissions.

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.

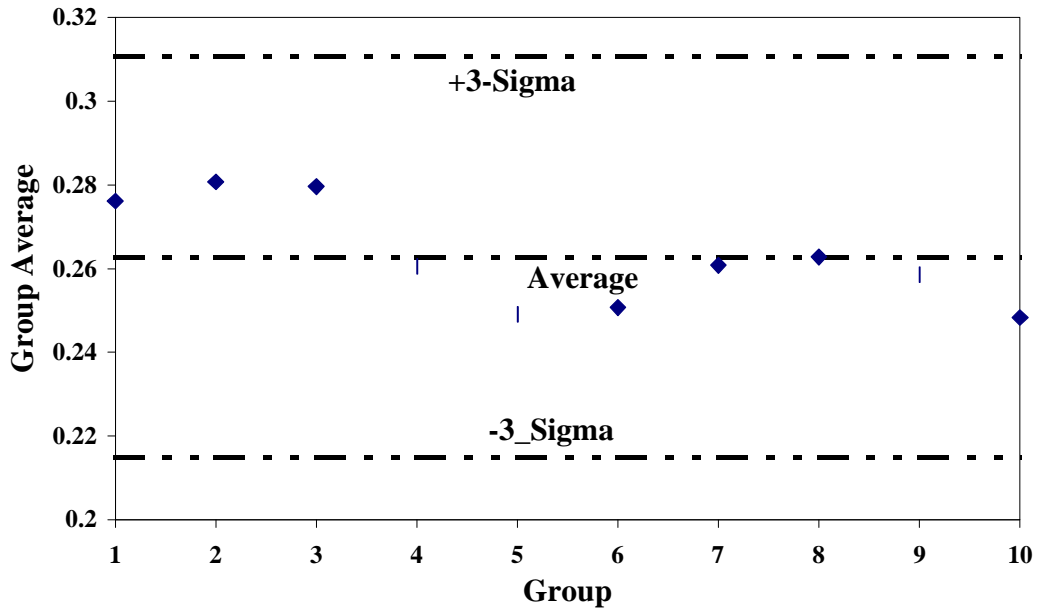


Figure 6. Shewhart Means Control Plot for PM.

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 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

This chapter describes emissions test results for biodiesel fuels obtained from IGT and those prepared by CIFER. 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 resealed.
- 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 test. 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 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 B), 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% max. 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 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 less 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, linoleates also produce much more NO_x.

Fuels Produced from Various Waste Fatty Acid Streams-(IGT Fuels)

Regulated Emissions:

Emissions results are presented in Table 18, along with the calculated coefficient of variation for repeated tests. 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. All neat biodiesels increased NO_x emissions relative to certification fuel. In particular, feedstocks containing unsaturated fatty acid chains (soy and canola) produce significantly higher NO_x emissions than more saturated materials.

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.

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

Table 18. Engine emissions data for various biodiesels and for bracketing runs with certification fuel.

| Run | Test Fuel | | bhp-h | THC | NO _x | CO | CO ₂ | 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 | 3.44% | 7104 |
| 4426 | Cert Fuel/Lot D-434 | H | 22.737 | 0.097 | 4.518 | 5.828 | 568.46 | 0.298 | 3.56% | 7130 |
| 4427 | Cert Fuel/Lot D-434 | H | 22.635 | 0.112 | 4.505 | 5.184 | 568.79 | 0.279 | 4.20% | 7424 |
| | | | Average | 0.105 | 4.574 | 5.521 | 567.88 | 0.284 | 3.73% | |
| | | | 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 | 5.71% | 7454 |
| 4429 | 20% Methyl Soy/80% Cert | H | 22.617 | 0.114 | 4.616 | 4.807 | 565.35 | 0.221 | 4.31% | 7410 |
| 4430 | 20% Methyl Soy/80% Cert | H | 22.656 | 0.114 | 4.610 | 4.864 | 567.26 | 0.221 | 2.86% | 7435 |
| | | | Average | 0.113 | 4.627 | 4.854 | 567.07 | 0.221 | 4.29% | |
| | | | 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 | 3.02% | 7413 |
| 4434 | 20%LFFAG/80% Cert | H | 22.714 | 0.088 | 4.702 | 5.133 | 565.68 | 0.224 | 3.40% | 7403 |
| 4435 | 20%LFFAG/80% Cert | H | 22.647 | 0.094 | 4.720 | 5.133 | 567.93 | 0.238 | 2.52% | 7432 |
| | | | Average | 0.093 | 4.709 | 5.153 | 566.65 | 0.229 | 2.98% | |
| | | | 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% | | |

Table 18. Continued.

| Run | Test Fuel | | THC | NO _x | CO | CO ₂ | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|-----------------------------|-------|--------------------|-----------------|--------------|-----------------|---------------|---------------|---------------------------|
| | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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 | 7737 |
| 4478 | 20%Inedible Tallow/80% Cert | H | 22.428 | 0.076 | 4.508 | 4.816 | 572.16 | 0.238 | 7364 |
| | | | Average | 0.069 | 4.510 | 4.986 | 586.40 | 0.236 | |
| | | | 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 | 7747 |
| 4518 | Cert Fuel/Lot D-434 | H | 22.476 | 0.132 | 4.588 | 5.194 | 573.24 | 0.301 | 7130 |
| 4519 | Cert Fuel/Lot D-434 | H | 22.646 | 0.124 | 4.666 | 5.806 | 570.45 | 0.311 | 6995 |
| 4520 | Cert Fuel/Lot D-434 | H | 22.565 | 0.123 | 4.637 | 5.530 | 571.13 | 0.315 | 6963 |
| | | | Composite | 0.127 | 4.695 | 5.703 | 578.10 | 0.313 | 6.78% |
| | | | Hot Average | 0.126 | 4.630 | 5.510 | 571.60 | 0.309 | 7.23% |
| | | | CoV% | 4.11% | 0.85% | 5.56% | | 2.26% | 61% |

Table 18. Continued.

| Run | Test Fuel | | THC | | NO _x | | CO | | CO ₂ | | PM | VOF, % of PM | Fuel Economy |
|------|------------------------|---|--------------------|---------------|-----------------|---------------|---------------|--------------|-----------------|---------|---------|--------------|--------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | btu/bhp-h | |
| 4524 | Methyl Soy Ester IGT | C | 22.298 | 0.082 | 5.853 | 4.401 | 605.95 | 0.093 | 20.34% | 7560 | | | |
| 4525 | Methyl Soy Ester IGT | H | 22.301 | 0.078 | 5.246 | 3.243 | 573.80 | 0.078 | 20.37% | 7279 | | | |
| 4526 | Methyl Soy Ester IGT | H | 22.226 | 0.074 | 5.233 | 3.334 | 575.45 | 0.080 | 25.00% | 7302 | | | |
| 4527 | Methyl Soy Ester IGT | H | 22.307 | 0.074 | 5.225 | 3.503 | 576.47 | 0.085 | 19.30% | 7318 | | | |
| | | | Composite | 0.076 | 5.323 | 3.509 | 579.63 | 0.083 | 21.38% | | | | |
| | | | Hot Average | 0.075 | 5.234 | 3.360 | 575.24 | 0.081 | 21.56% | | | | |
| | | | 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 | 25.00% | 7545 | | | |
| 4533 | Methyl Canola/Lot 9777 | H | 22.375 | 0.065 | 5.074 | 2.926 | 570.14 | 0.076 | 19.23% | 7203 | | | |
| 4534 | Methyl Canola/Lot 9777 | H | 22.410 | 0.070 | 5.096 | 2.997 | 568.20 | 0.074 | 12.50% | 7180 | | | |
| 4535 | Methyl Canola/Lot 9777 | H | 22.357 | 0.066 | 5.080 | 2.997 | 567.98 | 0.081 | 20.00% | 6658 | | | |
| | | | Composite | 0.069 | 5.178 | 3.129 | 572.61 | 0.081 | 18.35% | | | | |
| | | | Hot Average | 0.067 | 5.083 | 2.973 | 568.77 | 0.077 | 17.24% | | | | |
| | | | 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 | 14.04% | 7660 | | | |
| 4540 | Methyl Lard/Lot 9811 | H | 22.227 | 0.069 | 4.783 | 2.966 | 571.52 | 0.073 | 28.00% | 7317 | | | |
| 4541 | Methyl Lard/Lot 9811 | H | 21.406 | 0.077 | 4.594 | 2.168 | 605.76 | 0.065 | 27.78% | 7738 | | | |
| 4542 | Methyl Lard/Lot 9811 | H | 21.482 | 0.075 | 4.611 | 2.223 | 572.20 | 0.067 | 29.55% | 7311 | | | |
| | | | Composite | 0.077 | 4.765 | 2.660 | 585.13 | 0.072 | 26.38% | | | | |
| | | | Hot Average | 0.074 | 4.663 | 2.452 | 583.16 | 0.069 | 28.44% | | | | |
| | | | CoV% | 5.71% | 2.24% | 18.18% | | 6.07% | 3% | | | | |

Table 18. Continued.

| Run | Test Fuel | | Emissions | | | | | | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------------|---|--------------------|-----------------|--------------|-----------------|---------------|--------------|---------------|---------------------------|
| | | | THC | NO _x | CO | CO ₂ | PM | | | |
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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 | 17.46% | 7673 |
| 4556 | Inedible Tallow Lot 10996 | H | 22.263 | 0.069 | 4.690 | 2.744 | 560.45 | 0.064 | 27.87% | 7146 |
| 4557 | Inedible Tallow Lot 10996 | H | 22.258 | 0.066 | 4.694 | 2.707 | 561.79 | 0.069 | 18.46% | 7163 |
| | | | Average | 0.068 | 4.692 | 2.725 | 561.12 | 0.067 | 21.26% | |
| | | | 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 | 26.32% | 7577 |
| 4570 | Edible Tallow Lot 112597 | H | 22.167 | 0.061 | 4.642 | 2.899 | 563.58 | 0.068 | 29.79% | 7221 |
| 4571 | Edible Tallow Lot 112597 | H | 22.204 | 0.061 | 4.648 | 2.866 | 561.08 | 0.071 | 26.09% | 7189 |
| 4572 | Edible Tallow Lot 112597 | H | 22.196 | 0.058 | 4.650 | 2.811 | 560.05 | 0.070 | 20.69% | 7174 |
| | | | Composite | 0.059 | 4.712 | 2.978 | 565.68 | 0.071 | 25.63% | |
| | | | Hot Average | 0.060 | 4.647 | 2.858 | 561.57 | 0.070 | 25.52% | |
| | | | CoV% | 2.91% | 0.08% | 1.56% | | 2.23% | 18% | |

Table 18. Continued.

| Run | Test Fuel | | Table 18. Continued. | | | | | | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|--------------------------|---|----------------------|--------------|--------------|--------------|---------------|--------------|-----------------|------------------------------|
| | | | THC | NOx | CO | CO2 | PM | | | |
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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 | 28.95% | 7580 |
| 4586 | Methyl LFFA Grease Ester | H | 22.161 | 0.053 | 4.790 | 2.953 | 567.05 | 0.069 | 22.92% | 7215 |
| 4587 | Methyl LFFA Grease Ester | H | 22.138 | 0.055 | 4.827 | 2.951 | 567.79 | 0.066 | 20.00% | 7225 |
| 4588 | Methyl LFFA Grease Ester | H | 22.193 | 0.055 | 4.810 | 3.066 | 565.50 | 0.070 | 17.02% | 7198 |
| | | | Composite | 0.056 | 4.871 | 3.104 | 570.76 | 0.070 | 21.26% | |
| | | | Hot Average | 0.054 | 4.809 | 2.990 | 566.78 | 0.068 | 19.98% | |
| | | | 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% | | |

Table 18. Continued.

| Run | Test Fuel | | THC | | NO _x | CO | CO ₂ | PM | VOF, % of | Fuel |
|--------------------|--------------------------|---|--------|---------|-----------------|--------------|-----------------|--------------|---------------|---------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | PM | economy |
| 4685 | Methyl HFFA Grease Ester | H | 21.783 | * | 4.719 | 2.508 | 558.69 | 0.058 | 16.39% | 7204 |
| 4686 | Methyl HFFA Grease Ester | H | 21.818 | * | 4.744 | 2.406 | 557.21 | 0.057 | 12.90% | 7004 |
| 4687 | Methyl HFFA Grease Ester | H | 21.758 | * | 4.737 | 2.405 | 558.31 | 0.058 | 18.03% | 6903 |
| Hot Average | | | | | 4.733 | 2.440 | 558.07 | 0.058 | 15.78% | |
| 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% | | |

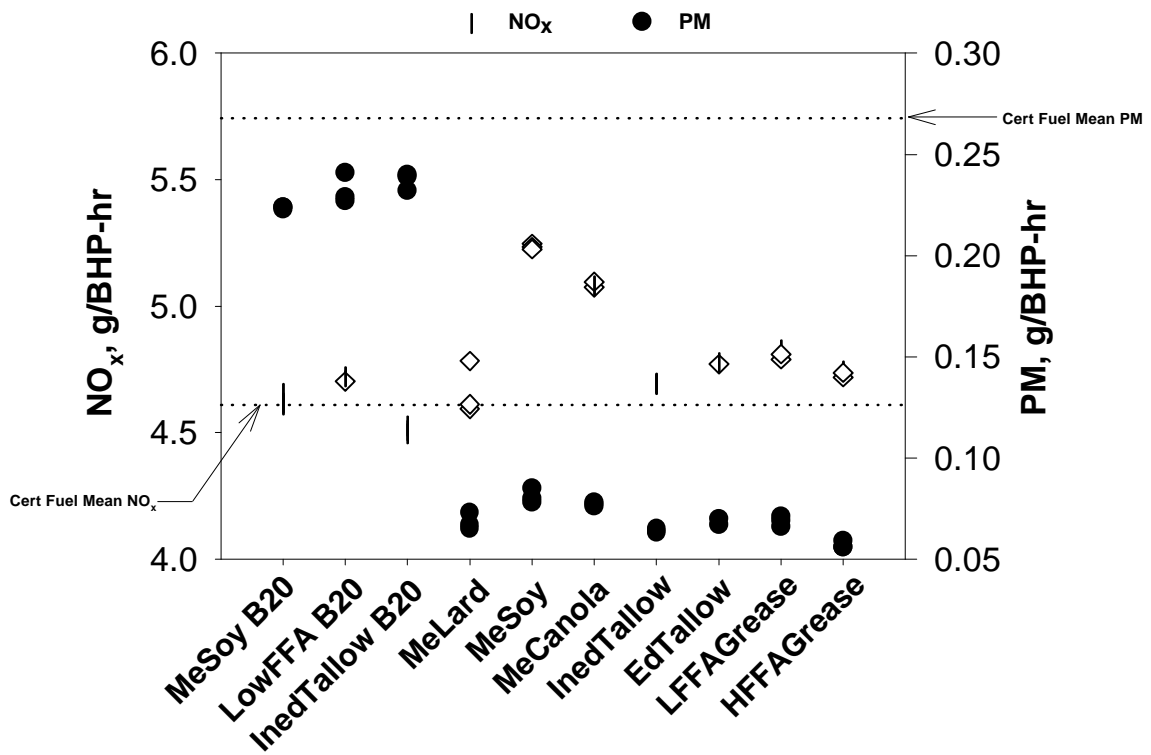


Figure 7. NO_x and PM Results for Testing of Various Neat Biodiesel and B-20 Blends.

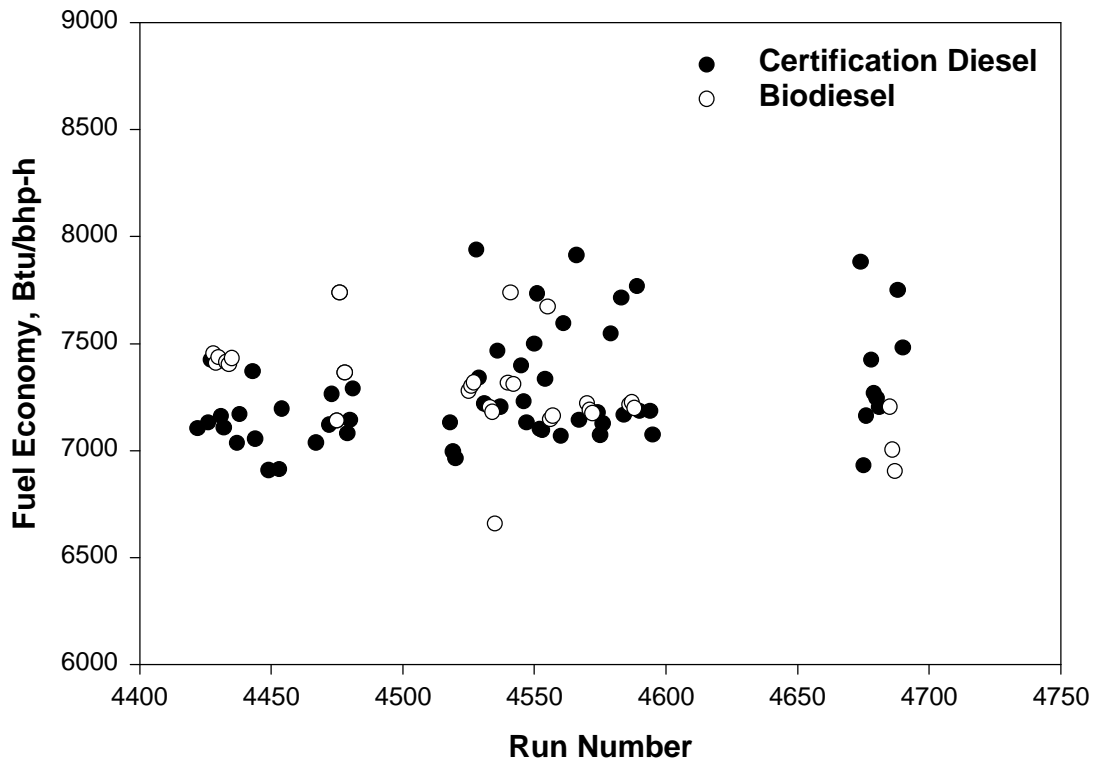


Figure 8. Btu Based Fuel Economy Comparison for Certification Diesel and Biodiesel Fuels.

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.

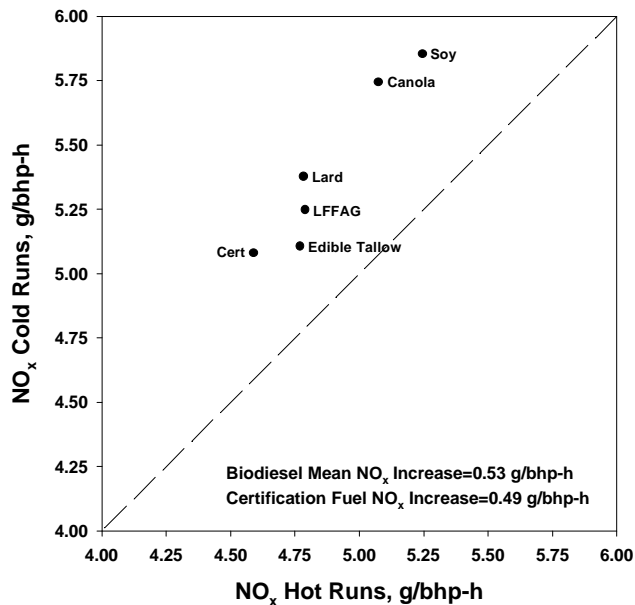


Figure 9. Comparison of Hot Start and Cold Start NO_x Emissions.

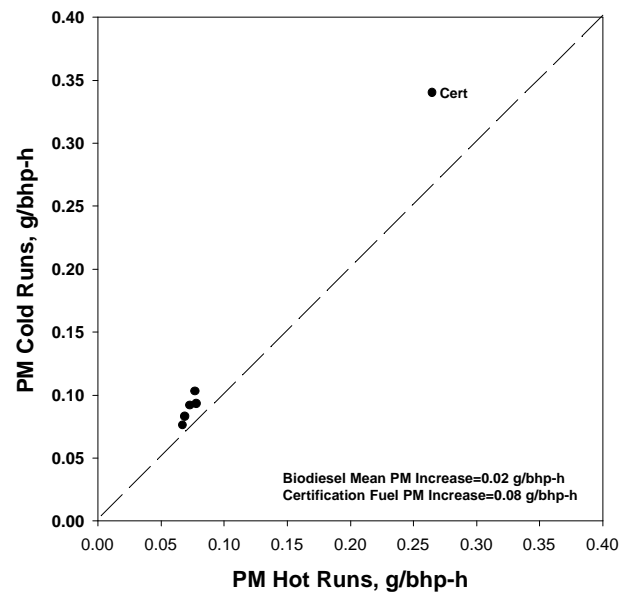


Figure 10. Comparison of Hot Start and Cold Start PM Emissions.

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% and 0.261 g/bhp-hr PM) is 0.0144 g/bhp-hr. For the biodiesels on average (21.4% and 0.07 g/bhp-hr), it is 0.0150 g/bhp-hr. The similar and very low emission rates suggests that the VOF is dominated by lubricating oil emissions. The indicated B20 VOF levels are not consistent with the VOF for the certification fuels and neat biodiesel. The indicated volatile emission for the B20 runs is lower than for certification fuel and neat biodiesel fuels.

Sulfate Emissions: Table 19 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.

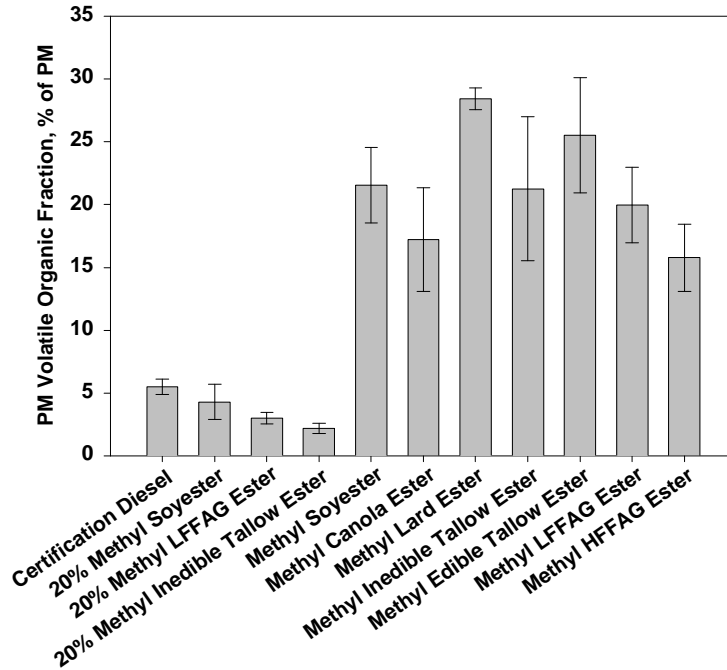


Figure 11. Volatile Organic fraction emissions for hot start runs as a percent of total PM.

Table 19. 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 20. 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 of 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 was exceptionally free 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.

Hydrocarbon Speciation: Attempts were made to perform chemical analysis of gaseous hydrocarbon, from both dilute and undiluted exhaust streams. The goal of this analysis was to determine emissions of the air toxics butadiene and benzene, as well as emissions of related compounds. This analysis turned out to be much more difficult than anticipated and the qualitative results obtained suggest no difference between certification diesel and biodiesel. However, experimental error for this data set is large and the results are not reported here as the absolute numbers do not appear to be meaningful.

We propose the following to address this situation. During the coming months we will be putting the DDC Series 60 engine back onto the engine test stand. We have retained roughly one drum of the same lot of certification fuel used in this study, as well as drums of the soy methyl ester and the HFFAG methyl ester. Before submission of a final report we will retest these three fuels and repeat emissions measurements for CO, THC, NO_x, PM, VOF, aldehydes, and speciation of gas phase hydrocarbons. We learned a great deal about how to perform this analysis (by failing to do it), and have spent considerable time of the past few months developing an improved method.

Table 20. 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

This section describes results of testing of biodiesels prepared from pure or nearly pure ester feedstocks, as well as several other fuels designed to examine specific aspects of fuel composition. Several of the fuels were solids at room temperature making engine testing challenging. Our approach was to heat the fuel tank and the engine test cell to temperatures high enough to melt these fuels. This was reasonably successful for methyl palmitate but was not particularly successful for methyl stearate or the methyl and ethyl esters of hydrogenated soybean oil.

Emissions data for these fuels is listed in Table 21. Figure 12 summarizes results for methyl ester fuels and Figure 13 for ethyl ester fuels. Note that in Figure 12 the NO_x and PM data points fall almost on top of one another for methyl palmitate. With the exception of methyl palmitate, methyl laurate, ethyl stearate and the ethyl ester of hydrogenated soybean oil all biodiesel fuels produced higher NO_x than certification diesel and 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.

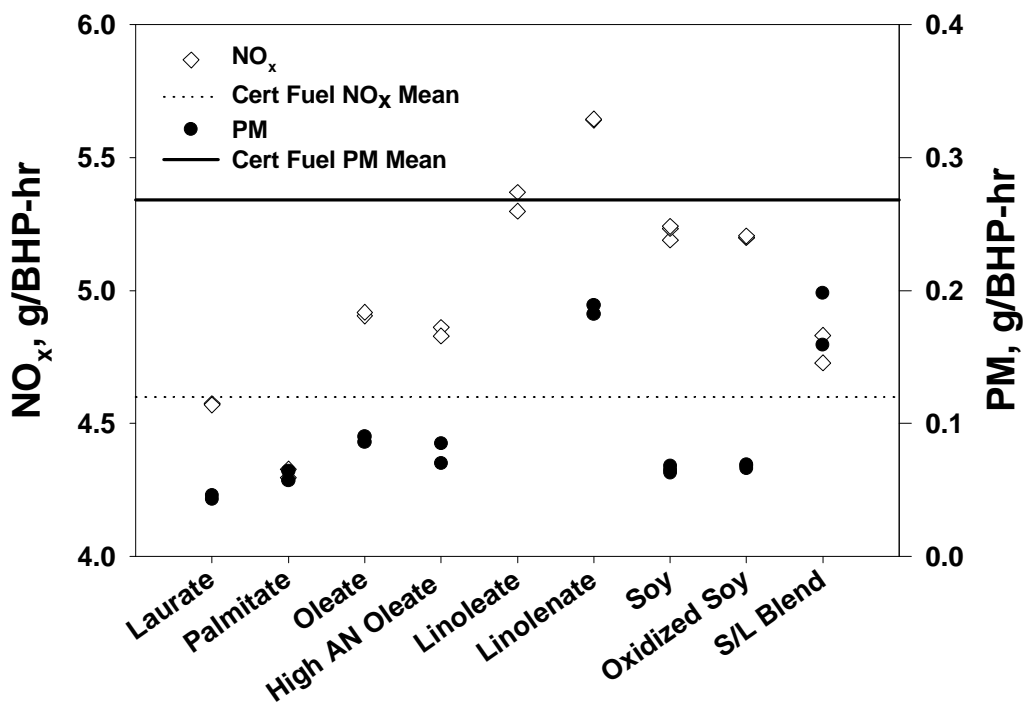


Figure 12. Summary of NO_x and PM Results for Methyl Ester Fuels.

Table 21. Emissions testing results for biodiesels prepared from pure or nearly pure feedstocks.

| Run | Test Fuel | | Emissions | | | | | | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------|---|----------------|---------------|--------------|--------------|----------------|--------------|--------------|---------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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% | | |
| 4467 | Cert Fuel/Lot D-434 | H | 22.434 | 0.097 | 4.538 | 5.752 | 573.553 | 0.301 | 7037 | |

Table 21. Continued.

| Run | Test Fuel | | THC | | NOx | CO | CO2 | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------|---|--------------------|--------------|--------------|--------------|----------------|--------------|--------------|---------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | | |
| 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% | | |

Table 21. Continued.

| Run | Test Fuel | | THC | | NOx | CO | CO2 | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------------|---|--------------------|----------------|--------------|--------------|----------------|--------------|--------------|---------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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 |

Table 21. Continued.

| Run | Test Fuel | | THC | | NOx | CO | CO2 | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------------|---|--------------------|---------------|--------------|---------------|----------------|---------------|-----------------|------------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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% | | |

Table 21. Continued.

| Run | Test Fuel | | THC | | NOx | CO | CO2 | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|---------------------------|---|--------------------|----------------|--------------|--------------|----------------|--------------|--------------|---------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | | |
| 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 |

Table 21. Continued.

| Run | Test Fuel | | THC | | NOx | CO | CO2 | PM | VOF, % of PM | Fuel Economy btu/bhp-h |
|------|-------------------------|---|--------------------|---------------|--------------|---------------|----------------|--------------|-----------------|------------------------------|
| | | | bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/bhp-h | g/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% | | |

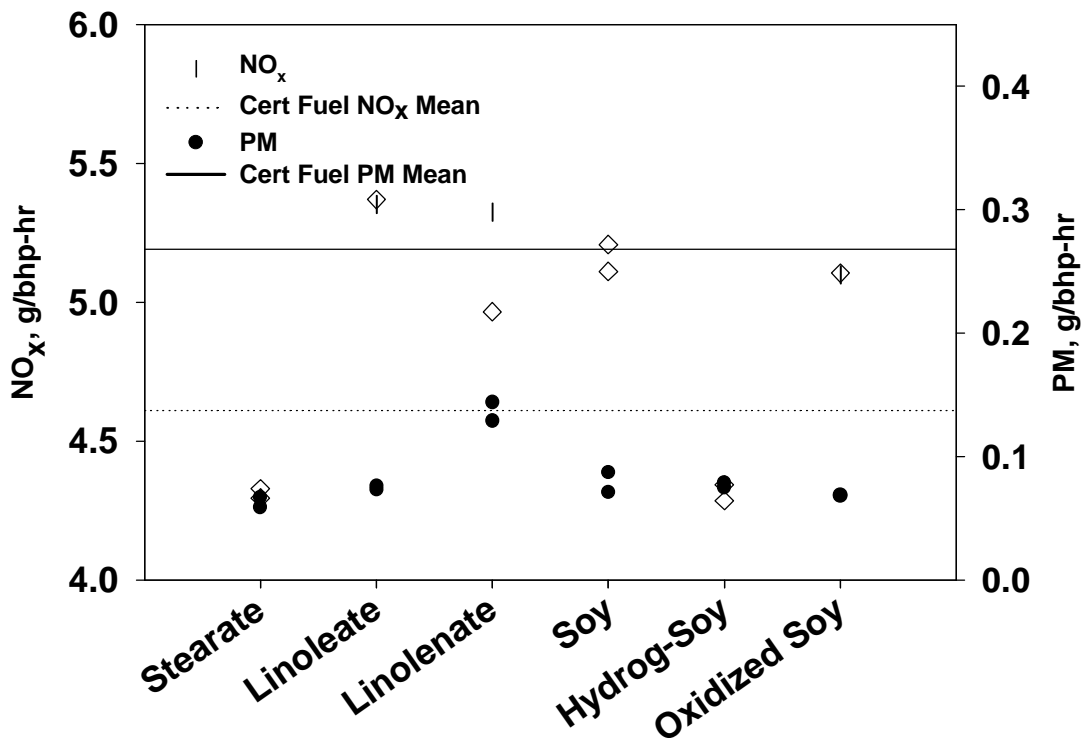


Figure 13. Summary of NO_x and PM Results for Ethyl Ester Fuels.

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. This oxidation occurred 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 the ethyl ester. From an emissions standpoint for the soyesters, 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 four fuels (soy, oxidized soy, linoleate, and stearate) 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 2 out of 4 tests compared to the methyl ester. Thus, *one can tentatively conclude that neat methyl and ethyl esters produced from the same base stock produce the same NO_x emissions.* Ethyl soyester PM emissions were 10.5% higher than methyl soyester emissions, but PM emissions were the same for ethyl and methyl esters of oxidized soy. Methyl stearate gave

higher PM than ethyl stearate, but only one valid run is available for the methyl ester and operability problems were encountered in running these fuels due to their high pour points. Overall, we tentatively conclude that PM emissions from ethyl and methyl esters are similar or the same.

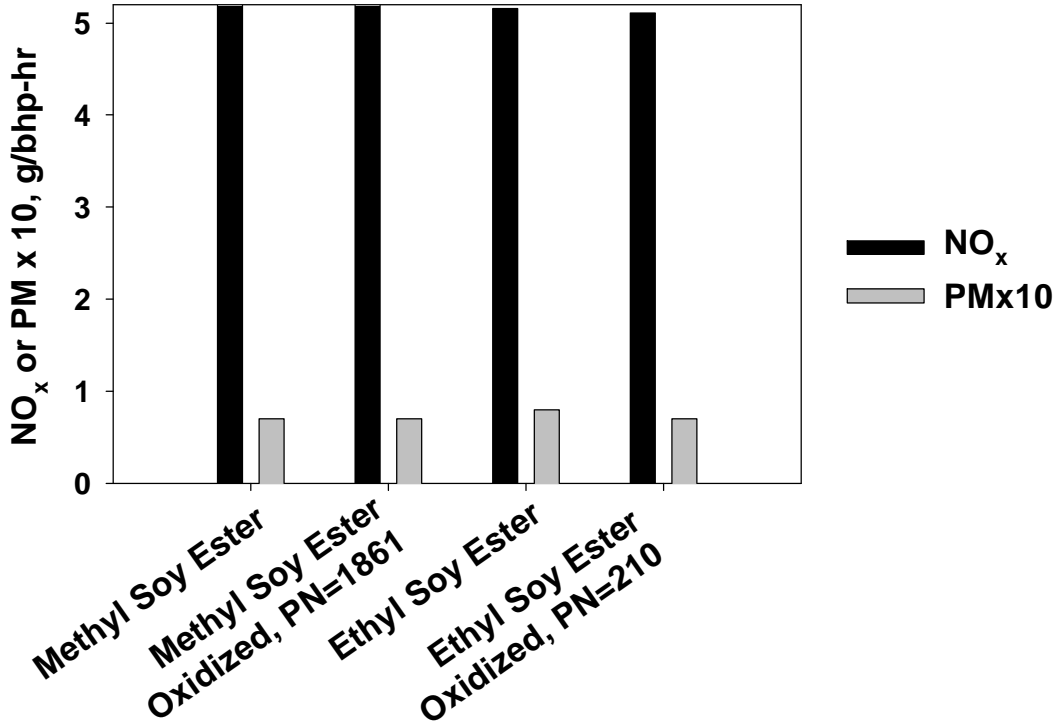


Figure 14. Effect of Oxidation of NO_x and PM Emissions from METHYL and ethyl Soyesters, PN=Peroxide Number.

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.

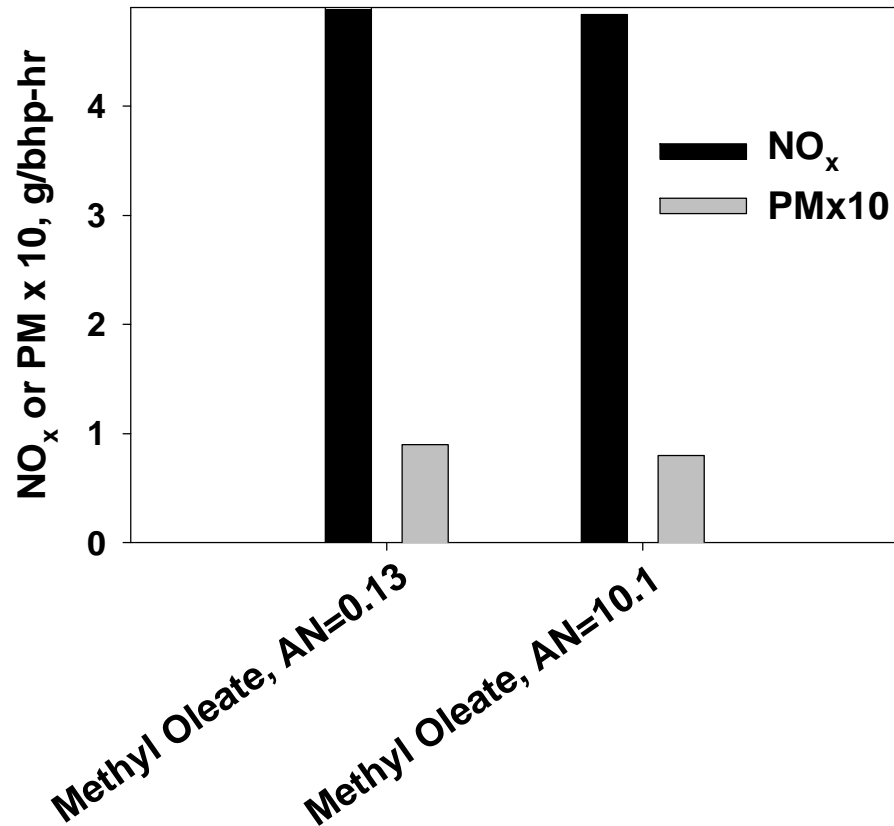


Figure 15. Comparison of NO_x and PM Emissions for Low and High Acid Number Methyl Oleate

Defined Blends:

A goal of the program was to produce define 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 Methyl linseed & 2 Methylstearate to simulate methyl oleate
- 2 methyl linseed & 1 Methylstearate 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 methyl linseed & 1 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: 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 22 provides a summary of property data used for modeling.

Table 22. 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 is concluded that the heating value is constant. 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 be deteriorated.

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 maldistribution 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 23. 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 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 23. 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 16 and Table 24 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.

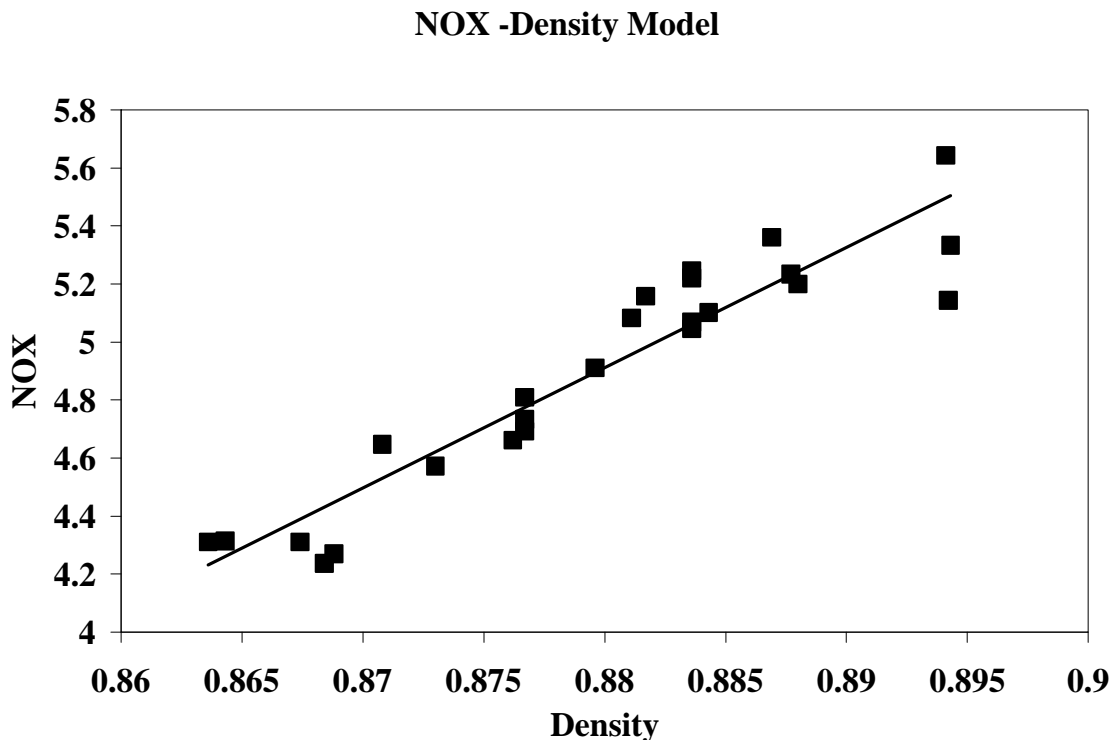


Figure 16. Relationship Between Density and NO_x Emissions.

Table 24. Regression Model for NO_x Emissions.

| <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 25 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 that fuel, all neat biodiesel fuels reduced particulate emissions compared to Number 2 diesel.

Table 25. 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 17 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

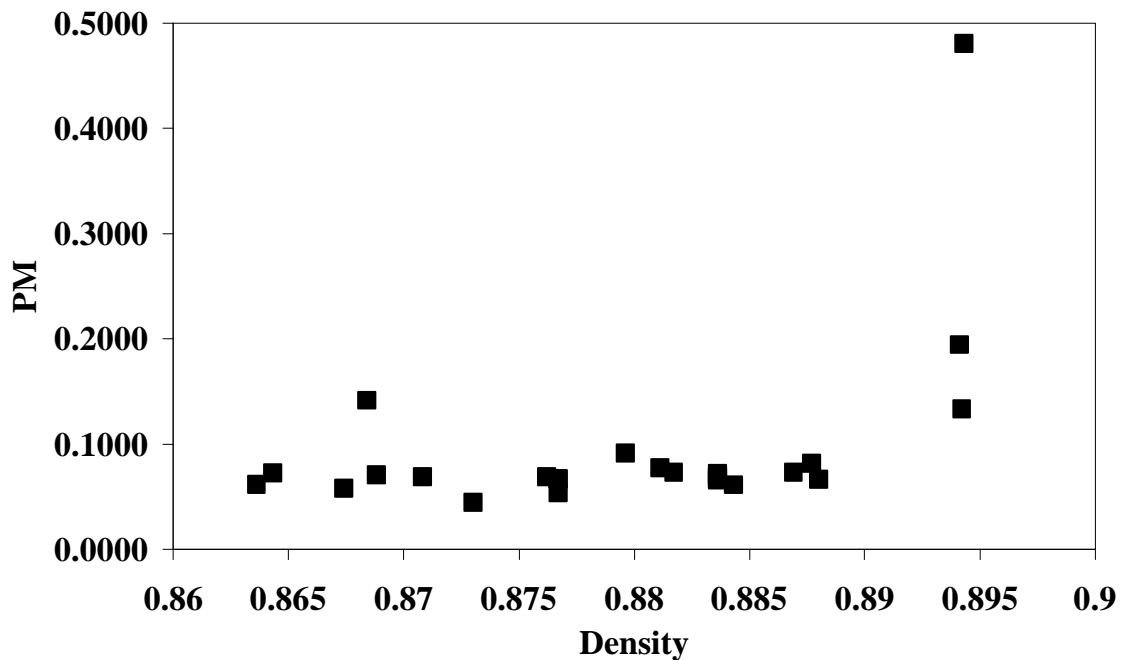


Figure 17. Relationship Between Fuel Density and PM Emissions.

To investigate whether the PM emissions are constant below the critical fuel density, a regression analysis was conducted with a modified data set which deleted 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 the fuel liquid during testing. The regression analysis is given in Table 26. 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 assumes constant PM emission of 0.070 g/bhp-hr as given in Table 27.

Table 26. Regression Model for Biodiesel PM Emissions.

| <i>Regression Statistics</i> | | | | | |
|------------------------------|--------------------------|-----------------------|----------------|----------------|-----------------------|
| | Adjusted R Square | 0.0510 | | | |
| | Standard Error | 0.0094 | | | |
| | Observations | 21 | | | |
| ANOVA | | | | | |
| | <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 27. 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

In this program, data were collected for 20% blends of several biodiesel fuels with certification fuel. Figures 18 and 19 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 19 shows the PM response to blending for this testing 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 28 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.

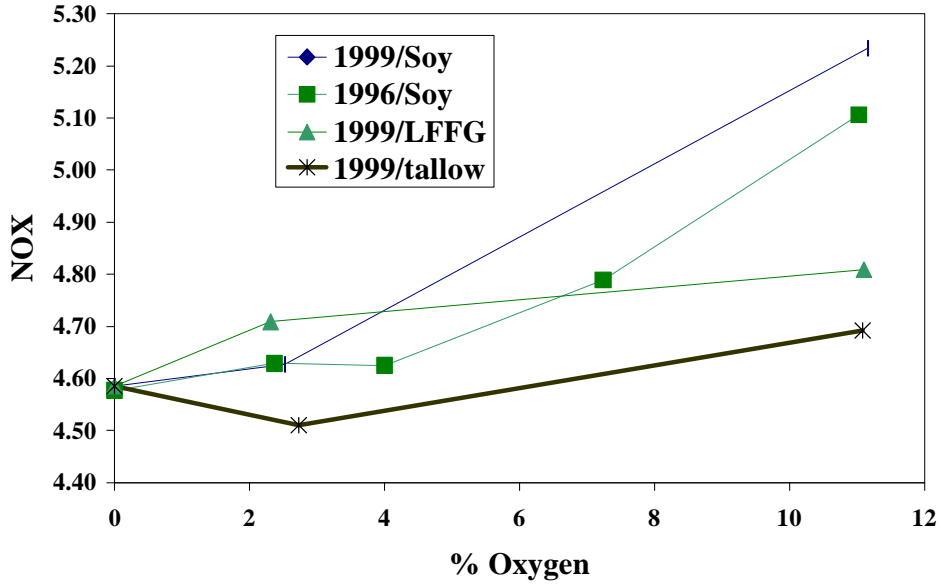


Figure 18. Effect of Fuel Oxygen Content on NO_x Emissions for Several fuels (1999 results from this study, 1996 results from Graboski, et al, 1996).

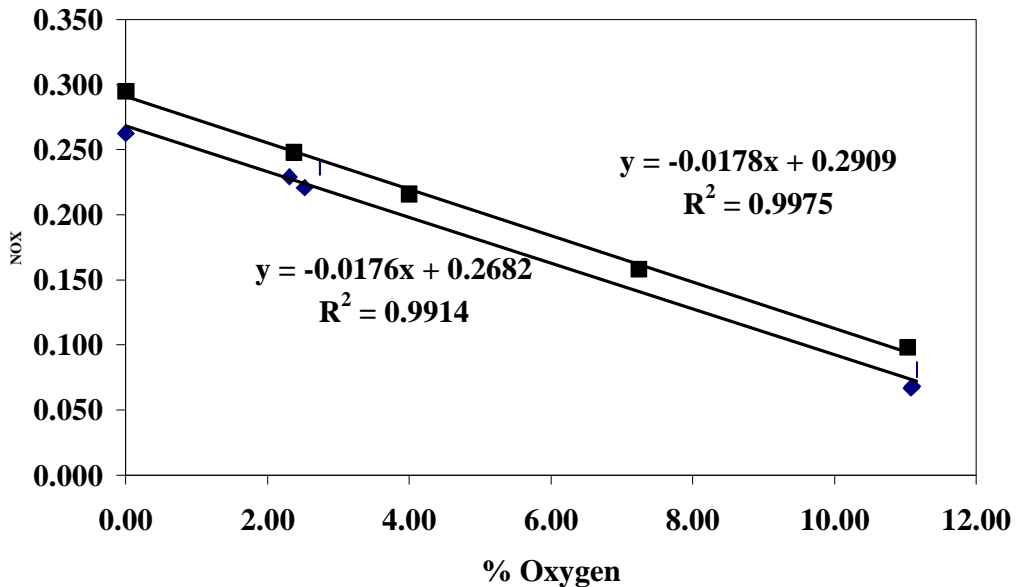


Figure 19. Regression Model Showing Effect of Oxygen on Particulate Matter.

Table 28. 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> | <i>Lower 95%</i> |
|--------------|---------------------|-----------------------|---------------|----------------|------------------|
| Intercept | 0.2895 | 0.0039 | 74.6950 | 0.0000 | 0.2809 |
| % Oxygen | -0.0175 | 0.0004 | -40.4717 | 0.0000 | -0.0185 |
| Test program | -0.0219 | 0.0040 | -5.4327 | 0.0002 | -0.0308 |

Discussion

This discussion is not dependent on whether pure esters or natural mixtures are considered. The correlation 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 20 shows how cetane number and density are related. As Table 23 demonstrated, there is a near perfect correlation between these properties. Cetane number can be used to discuss emissions effects. Figure 20 might suggest that neat biodiesels with cetane numbers greater than about 60 produce NO_x emissions equal to or less than certification fuel. In order to get the full PM benefit, the cetane number of the biodiesel needs to exceed about 45. The cetane requirement for low NO_x emissions is stronger than the demand for low PM emissions. PM appears impacted at cetane number values only less than present in 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 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 also 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 diesel engines will change the overall results but probably not the trends. For a more detailed discussion of engine effects see Graboski and McCormick, 1998.

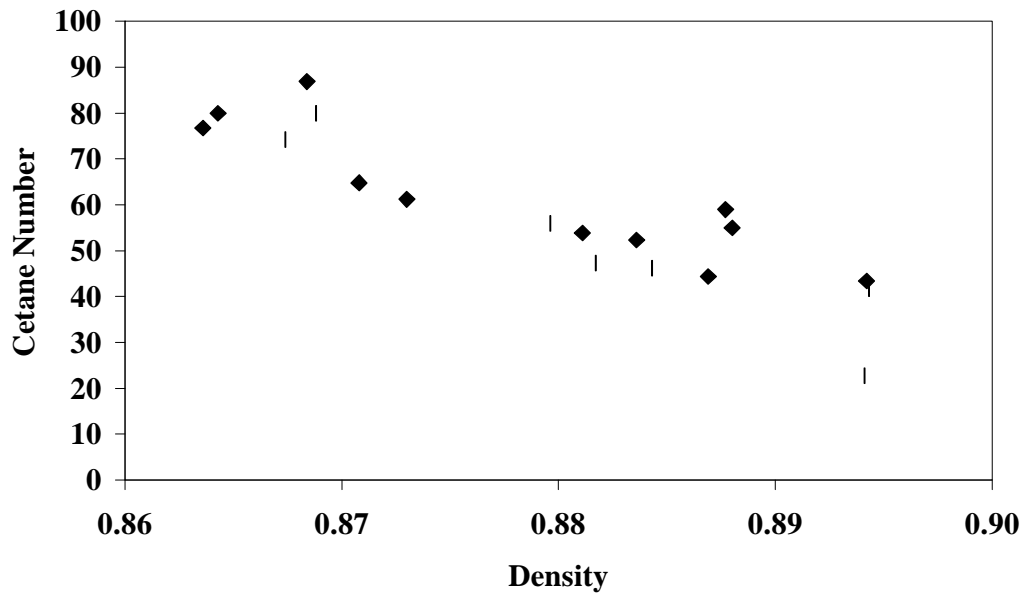


Figure 20. Relationship between cetane number and density.

Conclusions

The emissions of NO_x and PM for a large number of neat biodiesel fuels of varying chemical composition measured using a 1990 DDC Series 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, 27 neat biodiesels and 3 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 allows 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 PAH and biological activity analysis by the University of California at Davis were collected.

All fuels tested 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. 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 (+/-0.3%) with no significant drift over the 4 month test program. PM emissions averaged 0.261 g/bhp-h (+/-2.7%). 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.

Analysis indicated that emissions could be correlated by one parameter, either density or cetane number (which were highly correlated with each other). The results indicate that all biodiesel fuels lowered PM relative to certification diesel. PM reduction was proportional to oxygen content for biodiesels with a cetane number of greater than about 45. NO_x emissions varied significantly with fuel composition but were well correlated with biodiesel density. All biodiesels increased NO_x relative to certification diesel with the exception of methyl laurate, methyl palmitate, ethyl 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, 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.

REFERENCES

- CRC, "Handbook of Chemistry and Physics", 63rd edition, CRC Press, 1983
- Coordinating Research Council, "Chemical Methods for the Measurement of Unregulated Diesel Emissions - Carbonyls, Aldehydes, Particulate Characterization, Sulfates, PAH/NO₂PAH" CRC Report No. 551, (1987).
- Graboski, M.S., Ross, J.D., McCormick, R.L. "Transient Emissions From No. 2 Diesel and Biodiesel Blends in a DDC Series 60 Engine" **SAE 961166**, 1996.
- Graboski, M.S., McCormick, R.L. "Combustion of Fat and Vegetable Oil Derived Fuels in Diesel Engines" Progress in Energy and Combustion Science, 24 125 (1998).
- Liotta, F., Montalvo, D., "The Effect of Oxygenated Fuels on Emissions from a Modern Heavy-Duty Diesel Engine", **SAE 932734**, 1993.
- Mandel, J., "The Statistical Analysis of Experimental Data", page 82, Dover Publications, NY, 1964.
- McCormick, R.L., Ross, J.D., Graboski, M.S. "Effect of Several Oxygenates on Regulated Emissions from Heavy-Duty Diesel Engines" Environ. Sci. Technol., 31 1144 (1997).
- Miller, J.A.; Bowman, C.T. *Prog. Energy and Combustion Sci.* **1989**, *15*, 287.
- Nikanjam, M., "Development of the First CARB Certified California Alternative Diesel Fuel", **SAE 930728**, 1993.
- Ortech International, "Methyl Soyate Evaluation of Various Diesel Blends in a DDC 6V-92 TA Engine", Ortech Final Report # 93-E14-21, April 1993.
- Parker, T.E., private communication, 1996.
- Sato, J.; Konishi, K.; Okada, H.; Nioka, T. *21st Symposium on Combustion* **1986**, 695.
- Signer, M.; Heinze, P.; Mercogliano, R.; Stein, H.J. **SAE 961074**, 1996.
- Spreen, K.B., Ullman, T.L., Mason, R.L., "Effects of Cetane Number, Aromatics, and Oxygenates on Emissions From a 1994 Heavy-Duty Diesel Engine With Exhaust Catalyst", **SAE 950250**, 1995.
- Ullman, T.; Mason, R.; Montalvo, D. *Study of Cetane Number and Aromatic Content Effects on Regulated Emissions from a Heavy-Duty Engine*, Coordinating Research Council Contract VE-1; Southwest Research Institute: San Antonio, TX, 1990.

Ullman, T.L., Spreen, K.B., Mason, R.L., “Effects of Cetane Number, Cetane Improver, Aromatics, and Oxygenates on 1994 Heavy-Duty Diesel Engine Emissions”, **SAE 941020**, 1994.

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 |

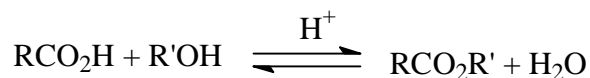
| | | |
|---------------------------|------------|----|
| Soygold | 03/22/1999 | 1H |
| 1:2 MeStearate:Me Linseed | 03/22/1999 | 2H |
| Cert Fuel/Lot D-434 | 03/22/1999 | 2H |
| Ethyl Stearate | 03/24/1999 | 2H |
| Cert Fuel/Lot D-434 | 03/24/1999 | 2H |
| Methyl Palmitate | 03/24/1999 | 2H |
| Cert 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 | 05/13/99 | 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:

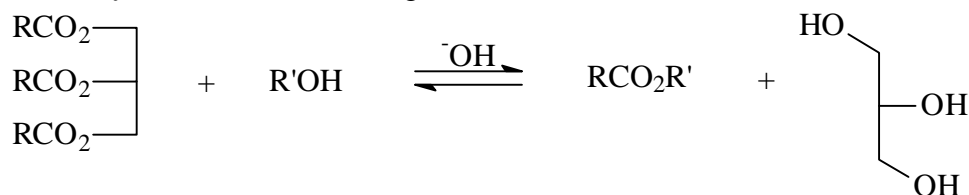


Methyl Oleate. Oleic Acid, technical grade (12 L, 37.8 Mol) and anhydrous methanol (4 L, 98.7 Mol) were stirred together and degassed under Ar_(g). Sulfuric acid (200 cm³, 3.7 Mol) was added over 10 minutes with a temperature gain of up to 10 °C. The mixture was stirred at reflux overnight and 75% of 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 $\text{Ar}_{(g)}$. Sulfuric acid (200 cm^3 , 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 cm^3). 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:



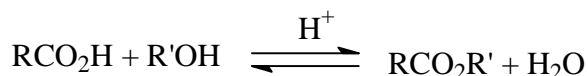
Methyl Linseed Ester. Linseed oil (12 L, 40.7 Mol) and methanol (4 L, 98.7 Mol) were stirred together and degassed under $\text{Ar}_{(g)}$. Sodium hydroxide (100 g, 2.5 Mol) was then added and the mixture stirred at reflux overnight. With the heating turned off, sulfuric acid (200 cm^3 , 3.7 Mol) was 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 $\text{Ar}_{(g)}$. 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 cm^3 , 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

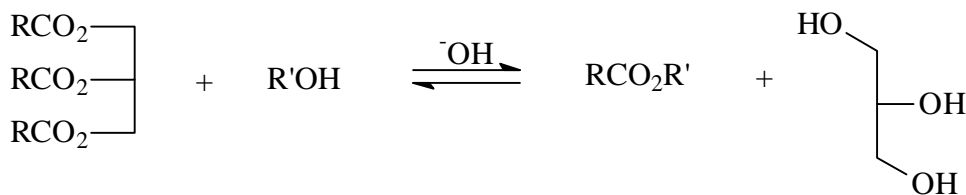
addition of sodium sulfate, a desiccant, resulted in no improvement of yield. This produced



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 $<0.8 \text{ mg KOH g}^{-1}$, the biodiesel standard. An acid number of $0.8 \text{ mg KOH g}^{-1}$ 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 distils 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 $2.6 \text{ mg KOH g}^{-1}$ after one distillation, $1.4 \text{ mg KOH g}^{-1}$ after two distillations and $0.8 \text{ mg KOH g}^{-1}$, 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 necessary to transesterify all fuels starting from vegetable oils three times to obtain a product that met the biodiesel 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, necessary 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 C: FUEL ANALYSIS REPORTS

APPENDIX D: FUEL ANALYSIS RESULTS REPORTED BY IGT

| <u>Test</u> | <u>LFFA</u> | <u>HFFA</u> | <u>Soy</u> | <u>Lard</u> | <u>Canola</u> | <u>Tallow</u> | <u>Inedible</u> <u>Tallow</u> |
|-------------------------------|--------------------------------|--------------------------------|------------|-------------|---------------|---------------|----------------------------------|
| | <u>Yellow</u> <u>Grease</u> | <u>Yellow</u> <u>Grease</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: 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).

