

THE EFFECT OF BIODIESEL FEEDSTOCK ON REGULATED EMISSIONS IN CHASSIS DYNAMOMETER TESTS OF A PICKUP TRUCK

C. L. Peterson, J. S. Taberski, J. C. Thompson, C. L. Chase

ABSTRACT. Six different vegetable oil esters (coconut ethyl ester, used hydrogenated soy methyl ester, rapeseed ethyl ester, mustard ethyl ester, safflower ethyl ester, and a commercial methyl ester of soy oil) were selected to represent a range of iodine numbers from 7.88 to 133. These vegetable oil esters were tested neat and in 20% biodiesel/80% diesel blends in comparison with low sulfur diesel fuel for the effect on regulated emissions. The test vehicle was a pickup truck with a 5.9 L turbo-charged and inter-cooled direct injection diesel engine. The emissions tests were conducted at the Los Angeles County Metropolitan Transit Authority Emissions Testing Facility on a chassis dynamometer. It was found that lower iodine numbers correlated with reduced nitrogen oxides (NO_x). As iodine number increased from 7.88 to 129.5 the NO_x increased 29.3%. Fatty acids with two double bonds appeared to have more effect on increasing NO_x emissions than did fatty acids with one double bond. Changes in carbon monoxide (CO), hydrocarbons (HC), and particulate matter (PM) were not linearly correlated with iodine number. It is apparent that the type of feedstock oil affects the characteristics of the biodiesel fuel. The most obvious difference is that the pour point changes with fatty acid composition, however, other fuel characteristics, some of which affect combustion, are also changed. This article reports on a study of biodiesel iodine number on changes in regulated emissions. The results of this and similar studies provide information for developing triglycerides specifically for optimum use in biodiesel. Modern chemical processes and/or plant breeding should make this possible.

Keywords. Biodiesel, Alternative energy, Vegetable oil, Feedstocks, Emissions, NO_x, Iodine number.

The use of biomass-based alternative fuels, including biodiesel, will improve the environment, reduce the use of petroleum reserves, and reduce foreign imports. Since 1979, University of Idaho personnel have researched the use of locally produced rapeseed oil as a diesel fuel substitute. While most biodiesel is produced with methanol and vegetable oil, the University of Idaho has developed techniques for using ethanol and vegetable oil, including waste french fry oil, to produce ethyl esters. Past research has shown that transesterified vegetable oils are very acceptable diesel fuel substitutes (Peterson, 1995, 1997, 1998). Many tests have shown these fuels to have characteristics as good as, or superior to, common diesel fuel. In spite of these excellent fuel characteristics, it is apparent that the choice of feedstock affects the characteristics of the fuel. It is crucial that before biodiesel can be recommended for general use,

that the effect of different fatty acid compositions on its combustion characteristics be well understood.

Vegetable oil esters have been reported to be cleaner burning than diesel fuel in a typical compression ignition (CI) engine. Feldman (1991) reported smoke opacities reduced as much as 70% for methyl ester of rapeseed oil compared to commercial diesel fuel. Hydrocarbons (HC) and carbon monoxide (CO) are reduced by as much as 50% (Peterson et al., 1996; Taberski et al., 1998). Most studies show that nitrogen oxides (NO_x), a regulated engine exhaust pollutant, is at about the same level when using conventional diesel fuel or biodiesel. Studies with PTO dynamometers generally show NO_x is increased compared to diesel fuel, studies with chassis dynamometers generally show NO_x is decreased in comparison to the same engine operated on diesel fuel. Particulate matter is known to increase with decrease in NO_x and vice versa, this same trend is observed with biodiesel.

The purpose of this study was to determine the effect of fatty acid composition, as identified by the iodine number, on regulated emissions. The study was conducted as part of a planned emissions study of a 1994 Dodge 2500 pickup truck with a 5.9 L turbo-charged and inter-cooled direct injection diesel engine which had been operated for 100,000 miles on rapeseed oil biodiesel and was being tested as part of the test termination.

The emissions tests were conducted at the Los Angeles County Metropolitan Transit Authority (LA MTA) Emissions Testing Facility (ETF) on a chassis dynamometer. The LA MTA conducts exhaust emissions tests in an effort to provide data to expand the use of clean air technology and alternate fuels in heavy-duty vehicles. The ETF, located in the greater Los Angeles area, is a state-

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of-the-art laboratory specifically designed and built for the purpose of collecting exhaust emissions data from heavy-duty vehicles during transient chassis dynamometer operations. In addition to supplying data to the scientific community and private customers, the ETF provides exhaust emissions testing and data to California regulatory agencies in an effort to support the development of new emissions regulations for heavy-duty vehicles. The ETF measures HC, CO, CO₂, NO_x, and PM. It is not a problem for diesel engines to meet the HC and CO requirements, and CO₂ is not a criteria pollutant. For these reasons, this article will concentrate on the effect of biodiesel feedstock on NO_x and PM.

LITERATURE REVIEW

After biodiesel's suitability and reliability in unmodified diesel engines was established, concern was focused on examining emissions characteristics of biodiesel fuel. The EPA currently only regulates hydrocarbons (HC), carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter (PM), and sulfur dioxide (SO_x). SO_x production is a function of the fuel not the engine design, and is not a problem with biodiesel since it has a very low sulfur content, so only the first four criteria pollutants are usually examined with biodiesel. However, unregulated mutagenic or toxic compounds and greenhouse gas emissions have become of increasing concern to researchers in anticipation of regulations related to these compounds (Chase et al., 2000).

HYDROCARBONS AND CARBON MONOXIDE

Hydrocarbon emissions are mostly the result of flame quenching in an internal combustion engine. There is a narrow quench zone near the cooled cylinder walls that makes the flame go out and the HCs are not burned. Carbon monoxide is partially combusted fuel. Because of this, HC and CO are typically very high on cold start due to colder engine parts quenching the flame and preventing complete combustion (Stone, 1992). Biodiesel will reduce both HC and CO compared to diesel in the same engine, under the same conditions (Peterson and Reece, 1996).

OXIDES OF NITROGEN

Nitrogen oxides (NO_x) collectively refers to both NO and NO₂. A colorless and odorless gas, NO gradually turns into NO₂ in air. Pure NO₂ is a poisonous, reddish-brown gas with a strong odor. Nitrogen oxides can cause mucous membrane irritation if exposed in high enough concentrations. Nitrogen oxides formation generally increases very strongly with increases in flame temperatures and slower flame speed. Nitrogen oxide emissions also increase with reduced engine speed. While high temperatures and pressures are desirable for high efficiency operation of a diesel engine, they are also prime conditions for the formation of NO_x gasses (Stone, 1992).

The NO_x emissions behavior of biodiesel in unmodified diesel engines varies in the literature. Several reports show NO_x is increased with biodiesel. However, in chassis dynamometer tests with the Cummins B 5.9 L, a reduction in NO_x with a corresponding increase in PM was found (Peterson and Reece, 1996a,b).

The variability in NO_x response for biodiesel may be due to individual variables in the engines themselves. Sharp (1996) stated that there is "a strong link between increasing cetane numbers and reducing NO_x emissions, but the response varies from engine to engine."

PARTICULATE MATTER AND SMOKE

Particulate emissions from diesel engines are typically much higher than spark ignition engines. Particulate matter consists largely of carbon soot particles, hydrocarbons partially absorbed by the soot, sulfates in the form of aerosols, and the soluble organic fraction (SOF). Soot particles are chains of carbon particles that have a large surface area where hydrocarbons can be deposited. These deposited compounds are mostly strong smelling aldehydes. It is widely believed that soot particles are especially harmful to human health because of these aromatic compounds in the soot and their small size. They are only a few ten-thousandths of a millimeter and can enter the lungs very easily (Adler, 1994).

Most researchers report reduced amounts of visible smoke and slightly less PM with biodiesel compared to diesel (Peterson and Reece, 1994). However, a detailed look at the transient emissions from a Cummins B 5.9 L diesel engine by Sharp (1996b) suggests that the observed reductions in smoke and particulate matter when fueled with biodiesel were due to carbon soot reduction while the mass of volatile organic fraction (VOF) increased. Sharp also observed, "The net decrease in total particulate using biodiesel fuels would have been larger but the increase in VOF partially offset the reduction in soot. An exhaust catalyst typically reduces the VOF of the particulates." This resulted in greater PM reduction efficiency from the catalyst when fueled with biodiesel due to the catalyst's greater effectiveness in reducing the VOF portion of the biodiesel particulate emissions.

FATTY ACID COMPOSITION

VanderGriend (1990) demonstrated differences in combustion of biodiesel using the KIVA computer model. Surface tension and specific gravity were important parameters for predicting spray patterns and the combustion process.

Peterson et al. (1997) compared ethyl and methyl esters of four biodiesel feedstocks on the basis of fuel characteristics and short-term engine performance tests. They reported a 25°C difference in pour points among the biodiesel fuels. They found injector coking was related to molecular weight and viscosity of the biodiesel. They also reported differences in smoke density based on feedstock.

Allen and Watts (1999) compared atomization characteristics of 15 biodiesel fuel types. They reported that viscosity and surface tension could be predicted from their fatty acid composition, and the atomization characteristics in turn could be predicted from the viscosity and surface tension.

Peterson (1994) observed that NO_x emissions from fueling with hydrogenated soy ethyl ester biodiesel (HySEE) with an iodine number of about 65 was lower (4% lower) than when fueling with rapeseed ethyl ester (REE) with an iodine number of about 115. This data was for a single run and it was not known at that time whether the data was significant.

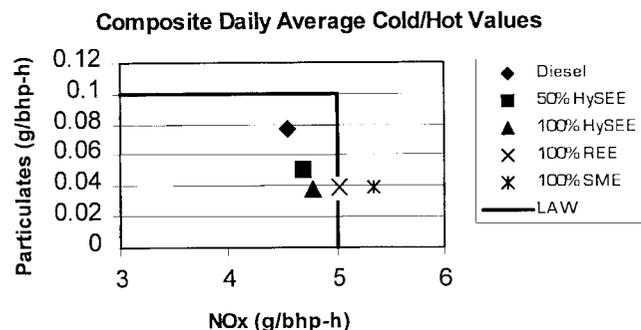


Figure 1—The PM-NO_x comparison from Smith (1998) for three biodiesel fuels and diesel.

Smith (1998) in tests with a 3406E Caterpillar engine reported similar findings (NO_x from HySEE was 6% lower than from REE). They also found that NO_x from soy methyl esters (SME) were 12% higher than REE. Particulate matter from each of the fuels was very similar. Figure 1 shows the familiar NO_x-PM box, the edges of the box are the 1998 Federal requirements for PM and NO_x. This data shows that NO_x from both 100% REE and 100% SME exceeded the federal limit.

McCormick et al. (1999) reported that biodiesel fuels with the lowest iodine numbers were closest to the diesel certification NO_x level. As iodine numbers increased, NO_x increased. They concluded that the presence of double bonds or higher iodine numbers appeared to be correlated with increasing NO_x emissions.

OBJECTIVES

The objective of this experiment was to test biodiesel fuels with a range of iodine numbers and determine the effect on regulated emissions including total HC, CO, NO_x, and PM, for each ester neat, 20% biodiesel/80% diesel blends, and low sulfur diesel fuel. Carbon dioxide levels were also measured.

MATERIALS AND METHODS

Biological and Agricultural Engineering at the University of Idaho (BAE) had a fuels analytical laboratory with equipment to test for heat of combustion, viscosity, flash point, cloud and pour point, density, specific gravity, API gravity, percent esterification, free glycerol, total glycerol, residual catalyst and alcohol content.

The University of Idaho Plant Science Department conducted tests for fatty acids. Phoenix Chemical Laboratory in Chicago, Illinois, was contracted to do the remaining fuel characterization tests including ash, cetane, water, and sediment. The facilities of Systems Lab Services in Kansas City were used to calibrate the free and total glycerol measurements of the University of Idaho lab.

EMISSIONS TESTING

The emissions tests were conducted at the Los Angeles Metropolitan Transit Authority Emissions Testing Facility located in Los Angeles, California, during March 1994 and November 1998. This facility has instrumentation to measure all regulated emissions: HC, CO, NO_x, and PM and although not regulated, CO₂. The ETF provides quality

assurance test results and calibrations in accordance with California Air Resources Board (CARB) quality assurance recommendations. (Dunlap, 1993, 1994; Peterson et al., 1996; Peterson and Reece, 1996).

The ETF is equipped with a single roll (6 ft diameter) chassis dynamometer capable of testing single-axle or dual-axle vehicles from 5,000 lbs to 100,000 lbs gross vehicle weight, and a computerized vehicle emissions testing system (VETS) consisting of an exhaust sampling dilution tunnel, analyzer and computer software to interface the sampling and analysis of the exhaust gas emissions. The facility, emissions sampling hardware and integral software were designed and built to meet the requirement of the Code of Federal Regulations 40 (CFR40), Part 86, "Control of air pollution from new and in-use motor vehicles and new and in-use motor vehicle engines: Certification and test procedures". The VETS is designed to perform exhaust emissions sampling and analysis to the requirements of the CFR for both compression ignition (CI) (diesel cycle) and spark ignition (SI) (Otto cycle) engines. This system permits the testing of vehicles over a variety of standardized operating conditions called drive cycles and a variety of vehicle load conditions.

EMISSIONS ANALYZERS

The ETF facility has been described in detail in several earlier articles (Dunlap, 1993; Peterson et al., 1996a,b) therefore only an overview will be provided here. The ETF's analytical system is composed of seven emissions analyzers. The HC analyzer uses the principle of hydrogen flame ionization to measure hydrocarbons, and includes a complete Heated Flame Ionization Detector (HFID). This analyzer offers proven reliability for diesel testing where high-boiling hydrocarbons are present.

Nitrogen oxides are measured using a chemiluminescent analyzer which monitors the chemiluminescent reaction of ozone (O₃) with nitric oxide (NO). Carbon monoxide and CO₂ are measured using non-dispersive infrared (NDIR) detection. The ETF analytical bench is equipped with a total of four NDIR analyzers and is therefore able to measure both low and high concentrations of CO and CO₂.

Particulate matter is collected during the entire test cycle by diverting a portion of the exhaust through a secondary dilution tunnel which contains collecting filters. The filters which have been conditioned and weighed prior to testing per the CFR requirements, are reweighed after the testing is completed to determine the amount of PM emissions in grams. The PM weight data are transferred to the VETS software where the grams per mile PM emissions data are generated based on exhaust flow through the filters for the applicable test.

TEST VEHICLE

The vehicle tested was a two wheel drive 1994 Dodge pickup truck with a direct injected, turbocharged and intercooled, Cummins B 5.9 L diesel engine. The vehicle had a five-speed manual transmission. The exhaust did not include a catalytic converter. The vehicle had accumulated 101,224 miles at the time of the test. The vehicle had been driven over 100,000 miles on 100% REE fuel including the required trip from Moscow, Idaho, to Los Angeles,

California, for the emissions test. Weight used during the test and for coast down was 3590 kg (7,900 lb).

The engine was not modified in any material way for use with the vegetable oil fuels. The fuel delivery system was modified for convenience of changing fuels between test runs. Fuel delivery and fuel return lines were broken and three-way, manually operated valves were installed so that stub lines with quick couplers could be installed on one part of the three-way valves. Individual 19 L (5 gal) fuel tanks were modified with fuel filter and flexible lines which could be connected to the three-way valves. During normal operation, fuel was delivered and returned to the vehicle tank. During testing the valves were switched to the external lines to which the correct test fuel was connected. For the tests, the fuel filter assembly mounted on the engine was removed and replaced with an aluminum block with internal connecting ports. This change was necessary to minimize the amount of fuel in the system when a fuel switch was required. Fuel filters were included on the individual fuel containers for each test fuel.

TEST DATA ANALYSIS

Emissions test data in units of grams per mile (gm/mile) are generated through the VETS for HC, CO, NO_x, CO₂, and PM. Fuel economy (FE) estimates were calculated and reported as described below. Three tests were completed for each fuel and one test for each fuel blend during the emissions tests. The exhaust emission data are recorded and reported through the VETS. It is noteworthy that no anomalies were observed and no driver error occurred during any phase of this test program.

TEST CYCLES

The test cycle used was the EPA Dynamometer Driving Schedule for Heavy-Duty Vehicles (Code of Federal Regulations 40, Part 86, Appendix 1, Cycle D) (EPA) (fig. 2). The EPA cycle has a total time of 1060 s.

FUELS TESTED

Fuels tested included Phillips D2 low-sulfur diesel control fuel (DIESEL or 2-D), 100% Coconut ethyl ester (100CCEE), 20% CCEE - 80% diesel (20CCEE), 100% Used Hydrogenated Soy ethyl ester (HySEE), 20% HySEE - 80% diesel (20HySEE), 100% Rapeseed ethyl ester (REE), 20% REE - 80% diesel (20REE), 100% Yellow mustard ethyl ester (MEE), 20% MEE - 80% diesel (20MEE), 100% Soy Methyl Ester (SME), 20% SME -

80% diesel (20SME), 100% Safflower oil ethyl ester (SFEE), and 20% SAFF - 80% diesel (20SFEE).

The ethyl esters were produced in the BAE Laboratory at the University of Idaho. The soy methyl ester was purchased from a commercial biodiesel supplier (Ag Environmental Products, Kansas City, Missouri). Fuel characterization data according to ASAE EP552 (ASAE, 1996) are provided in table 1. Fatty acid distribution of the biodiesel feedstocks are shown in figure 3. Cetane numbers, as measured by Phoenix Chemical Laboratory, Chicago, Illinois, for each of the neat biodiesel fuels, the 20% blends and diesel are shown in figure 4.

FUEL MASS FLOW RATE

Fuel consumption was determined by direct weighing. The fuel containers were placed on an electric scale accurate to the nearest 0.02 lb. The weight of fuel was read at the start and end of each test.

EXPERIMENTAL DESIGN

Only a limited time was available for these tests at the ETF. Each of the neat fuels were used in three replicates of hot start tests. The REE, HySEE, and SME had one cold start each. Hot starts for the blends were conducted as follows: single replicates of the 20% blends for CCEE and SME, two replicates of the 20% blend for HySEE, and three replicates of the 20% blend for REE.

RESULTS AND DISCUSSION

Table 1 provides the fuel characterization data for the Six Biodiesel Feedstocks, the 20% blends and the low sulfur reference diesel fuel used in the emissions tests. Table 2 is the correlation coefficients defining the relationships between several of the fuel characteristics for the biodiesel fuels. The blends and diesel fuel were not included in the correlation analysis. Eighteen of the correlations are above 0.80, and 11 correlations were above 0.90. Several of the correlations such as the one double bond, two double bonds with iodine number would be expected. If one ignores those the correlations of interest are iodine number with specific gravity (0.884), viscosity with flash point (-0.841), viscosity with molecular weight (0.940), viscosity with heat of combustion (0.924), viscosity with total glycerol (-0.814), and heat of combustion with total glycerol (-0.949). (One should interpret these correlations carefully. In this test total glycerol was higher for the low molecular weight feedstocks which have a low viscosity, hence there was a negative correlation of total glycerol with viscosity. In a single feedstock, however, the correlation may be different.) Note that small increases in total glycerol tend to reduce the viscosity and heat of combustion. Presence of double bonds in the fatty acids tend to increase viscosity, specific gravity and heat of combustion. Total esterification was more difficult with lower carbon chain lengths as evidenced by a slight increase in total glycerol in the sample. Figure 5 is a plot of cetane number versus iodine number for the six test fuels. The correlation coefficient between cetane and iodine as measured in these tests was -0.597.

Figure 6 and 7 show the fuel consumption data for each of the fuels taken during the hot start and cold start tests.

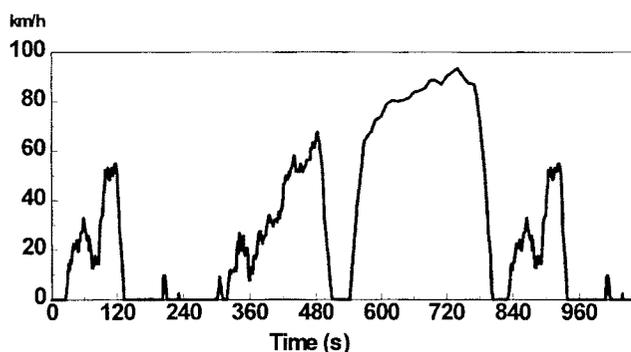


Figure 2—The EPA dynamometer driving schedule for heavy duty vehicles used for the emissions tests.

Table 1. Fuel characterization data for six biodiesel feedstocks, 20% blends and diesel included in LA MTA chassis dynamometer emissions tests

Lab Tests	D2	REE	20 REE	HySEE	20 HySEE	SME	20 SME	Coco EE	20 CocoEE	Saff EE	Must EE
Iodine no.	5.97	92.5	23.28	65.2	17.82	129.5	30.68	7.88	6.35	133.1	98
Viscosity (cSt)	2.662	6.024	3.1	5.54	3.1	3.992	2.88	3.085	2.71	4.307	5.656
Heat of comb (Btu/lb)	19340	17482	19118	17237	19037	17091	18981	16405	18915	17142	17489
Sp. gr. @ 15° C	0.848	0.874	0.853	0.875	0.854	0.885	0.856	0.87	0.852	0.884	0.875
Free glycerin (wt.%)	na	0.001		0.001		0.017		0.022		0.001	0.002
Total glycerin (wt.%)	na	0.136	0.093	0.239	1.027	0.188	0.103				
Cloud point (°C)	-15	1	-13	7	-9	1	-11	5	-7	-6	1
Pour point (°C)	-18	-12	-15	6	-9	0	-12	-3	-15	-6	-15
Flash point (°C)	77	170	79	174	79	185	78	190	79	178	183
Potassium (ppm)	na	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Water & sed (%)	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02	< 0.02
Cetane	46.5	67.4	53.5	65.1	54.9	55.9	51.6	67.4	54.9	62.2	54.9
Fatty acid (%)											
Lauric (12:0)								54.9			
Myristic (14:0)								20.9			
Palmitic (16:0)		2.7		11.5		10.3		10.5		6.4	2.8
Stearic (18:0)		1.1		12.3		4.3		3.3		2.5	1.2
*trans (18:1)				28.6							
Oleic (18:1)		12.8		29.1		22.8		7.8		13.5	26.1
*				8.4							
*				2.2							
Linoleic (18:2)		11.1		3.3		53.1		2.1		75	9.8
Linolenic (18:3)		8.1		0.2		7.6					10
Eicosanoic (20:1)		7.7		0.2							10.6
Erucic (22:1)		49.6		0.3							33.1
Nervonic (24:1)		0.9									2.2

* Material not in the GC calibration list.

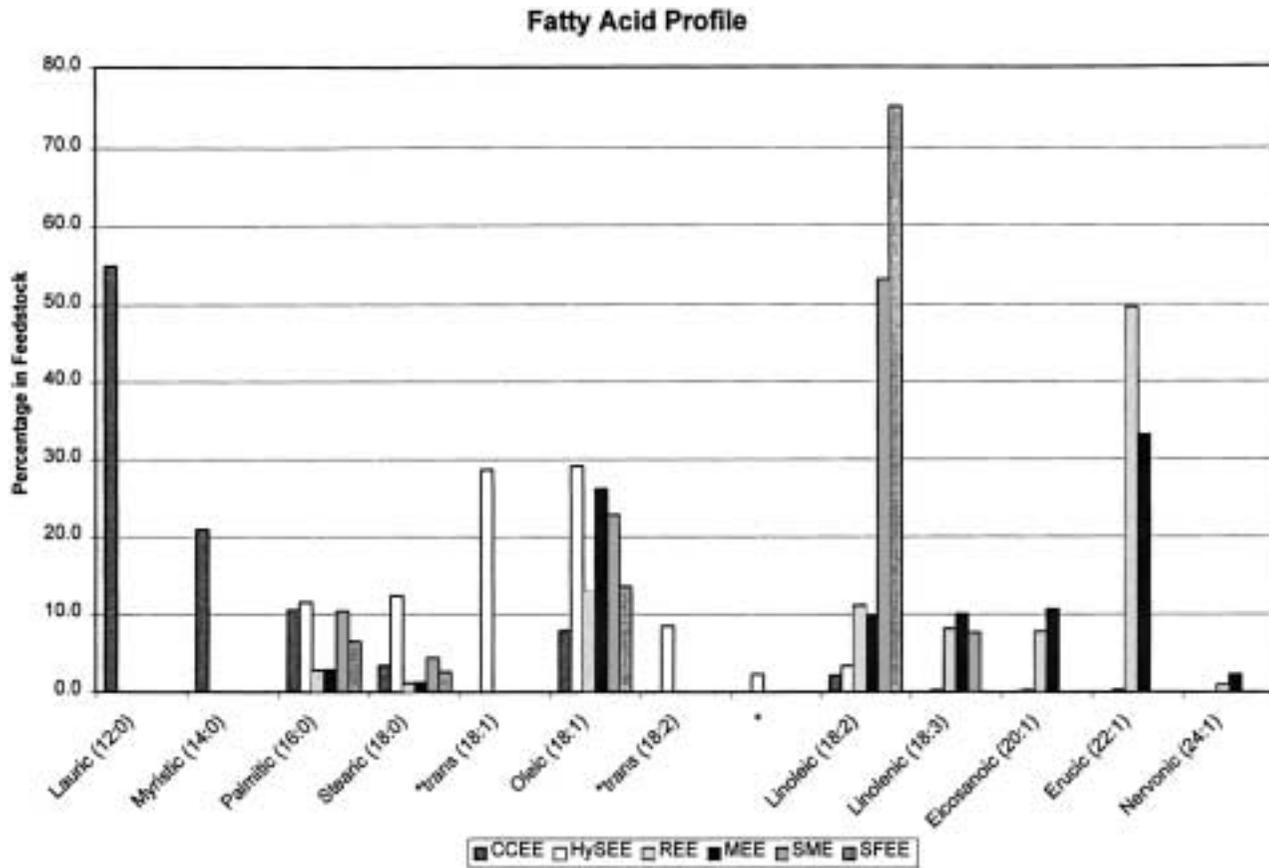


Figure 3—Fatty acid distribution in the six biodiesel feedstocks.

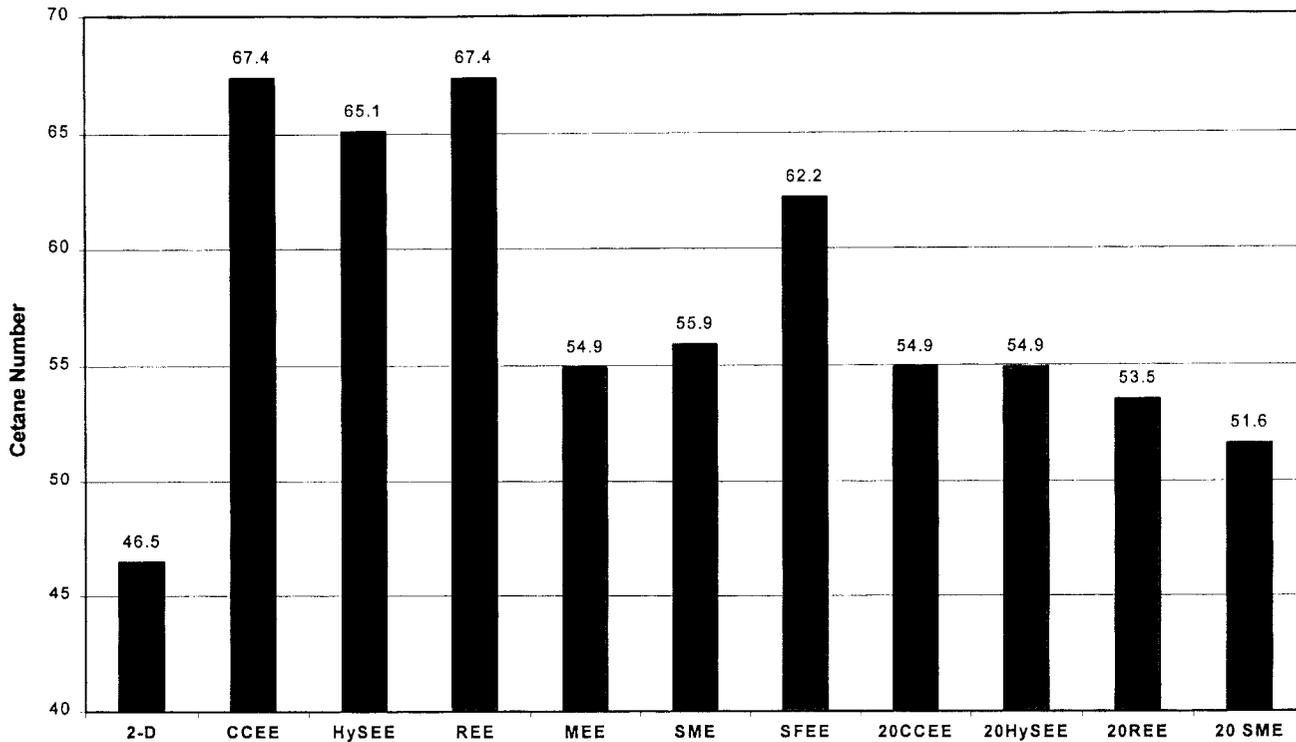


Figure 4—Cetane numbers for the six biodiesel fuels, the 20% blends, and diesel.

Table 2. Correlation coefficients defining the relationship between several fuel characteristics for six biodiesel feedstocks included in LA MTA chassis dynamometer emissions tests

Char.	Iodine	Pour	Flash	SG	Cetane	Total Glycerol	MW	Viscosity	H of C	One*	Two*	Three*	Comb†	Comb23‡
Iodine	1.000													
Pour	-0.229	1.000												
Flash	-0.435	0.190	1.000											
SG	0.884	0.137	-0.119	1.000										
Cetane	-0.597	0.150	-0.270	-0.584	1.000									
Total glycerol	-0.806	0.203	0.752	-0.526	0.424	1.000								
MW	0.605	-0.596	-0.789	0.171	-0.238	-0.871	1.000							
Viscosity	0.377	-0.409	-0.841	-0.052	-0.060	-0.814	0.940	1.000						
H of C	0.693	-0.448	-0.780	0.305	-0.347	-0.949	0.978	0.924	1.000					
One*	0.158	-0.436	-0.662	-0.276	-0.076	-0.646	0.846	0.948	0.815	1.000				
Two*	0.779	0.042	-0.038	0.931	-0.398	-0.320	0.034	-0.230	0.116	-0.480	1.000			
Three*	0.373	-0.630	-0.224	0.033	-0.490	-0.471	0.671	0.579	0.652	0.685	-0.168	1.000		
Comb	0.916	-0.433	-0.651	0.627	-0.505	-0.934	0.872	0.704	0.918	0.531	0.483	0.588	1.000	
Comb23	0.845	-0.051	-0.072	0.950	-0.477	-0.395	0.135	-0.146	0.215	-0.385	0.989	-0.021	0.578	1.000

* One, two, and three refer to the percent of fatty acids containing one, two, and three double bonds in the biodiesel feedstock.

† Comb refers to the combined percentage of of fatty acids containing one, two, and three double bonds in the feedstock.

‡ Comb23 refers to the combined percentage of of fatty acids containing two, and three double bonds in the feedstock.

The data is provided in terms of weight of fuel per run. Each run was 5.56 ± 0.02 miles in length.

Table 3 shows the average emissions data for each neat test fuel. Means for HC, CO, NO_x, and PM were statistically highly significantly different between fuels. Tukey's mean separation test is included in the table. It can be observed that while each of the compounds were different for the various fuels, only NO_x had a predictable increase based on iodine number. The CO₂ means were not significantly different for any of the tests and no further analysis for this compound will be included.

Table 3 provides cold start emissions data for four of the biodiesel feedstocks and diesel. Because of time restraints on the test cell only one replication of each cold start test

was included which precludes statistical analysis. The cold start data also shows increasing NO_x with increasing iodine number.

Table 4 provides hot start means for HC, CO, CO₂, NO_x, and PM for each of the biodiesel fuels with the exception of mustard in a 20% blend with diesel. No statistics are shown because of insufficient replications, but again NO_x increases with increasing iodine number in the biodiesel feedstock. The NO_x from SME is 29.3% higher than from CCEE and NO_x for SFEE is 31.2% higher than for CCEE.

The only regulated emission found to be significantly influenced by iodine number was NO_x. The data for HC,

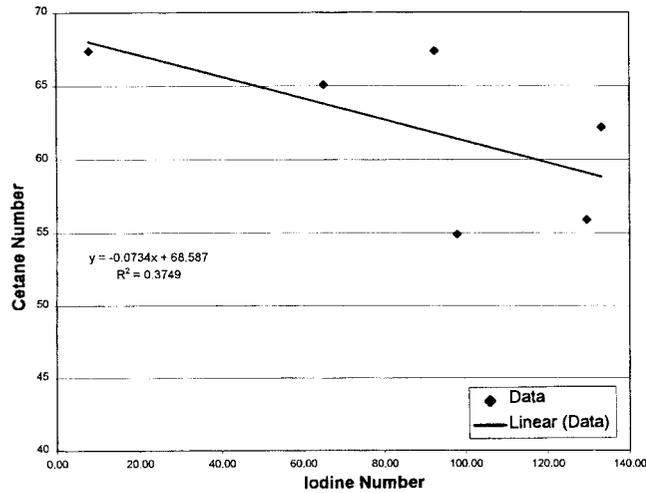


Figure 5—Iodine number and cetane number comparison for the six biodiesel fuels. A linear regression line is shown through the data points ($R^2 = 0.375$).

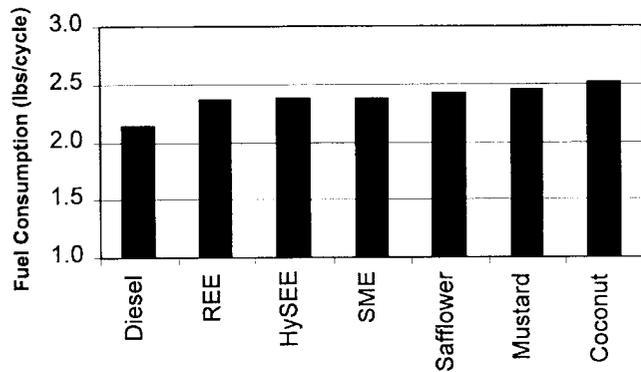


Figure 6—Fuel consumption for the six biodiesel feedstocks and diesel during the hot start emissions tests. Each test run was 9.0 km \pm 0.32 km (5.6 mile \pm 0.2 mile).

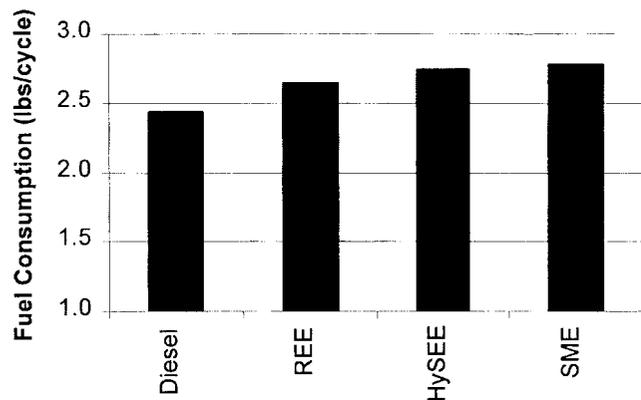


Figure 7—Fuel consumption for the three biodiesel feedstocks and diesel during the cold start emissions tests. Each test run was 9.0 km \pm 0.32 km (5.6 mile \pm 0.2 mile).

CO, and PM for the neat fuels for both cold starts and hot starts is provided for information.

HC

Figures 8 and 9 show the cold start and hot start data respectively for the hydrocarbons emission. While HC

Table 3. Hot start means for HC, CO, CO₂, NO_x, and PM LA MTA chassis dynamometer emissions tests for six biodiesel feedstocks (gm/mile)

Biodiesel	HC	CO	CO ₂	NO _x	PM
CCEE	0.538ab*	2.160ab	654.0a	4.570a	0.116d
HySEE	0.392ab	2.000b	641.0a	4.915ab	0.243ac
REE	0.294b	2.150ab	636.3a	5.300b	0.180cd
MEE	0.479ab	2.225ab	672.3a	5.780c	0.267ab
SME	0.632a	3.295a	539.8a	5.910c	0.246bc
SFEE	0.588a	3.103ab	658.1a	5.997c	0.268a
2-D	1.171c	4.553c	673.3a	5.960c	0.157d

* Means followed by the same letter are not significantly different according to Tukey's test ($P \leq 0.05$).

Table 4. Cold start for HC, CO, CO₂, NO_x, and PM LA MTA chassis dynamometer emissions tests for three biodiesel feedstocks (insufficient replications for statistical comparisons; gm/mile)

Biodiesel	HC	CO	CO ₂	NO _x	PM
HySEE	0.651	3.970	744.9	5.410	0.320
REE	0.619	4.520	708.6	5.800	0.305
SME	1.817	8.420	735.4	6.240	0.887
2-D	4.342	11.210	714.0	6.340	0.970

Table 5. Hot start means for HC, CO, CO₂, NO_x, and PM LA MTA chassis dynamometer emissions tests for 20% blends of four biodiesel feedstocks and diesel (gm/mile)

Biodiesel	HC	CO	CO ₂	NO _x	PM
CCEE	0.902	3.270	611.2	5.210	0.137
HySEE	0.822	2.910	659.3	5.615	0.167
REE	0.745	2.893	642.5	5.777	0.139
SME	1.061	3.900	615.0	5.660	0.164
2-D	1.171	4.553	673.3	5.960	0.157

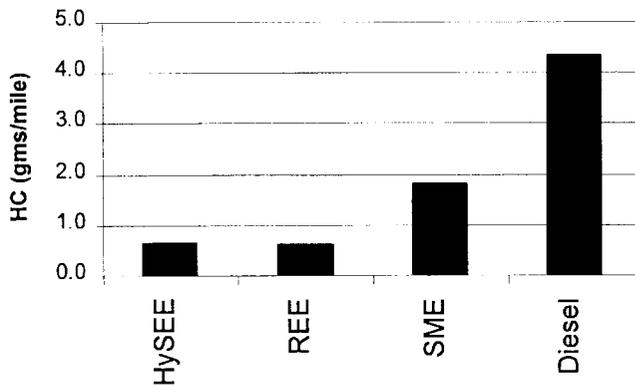


Figure 8—HC for the three biodiesel feedstocks and diesel during the cold start emissions tests.

differences were significant between fuels, a consistent relationship with iodine number for HC was not observed.

CO

Figures 10 and 11 show the cold start and hot start data respectively for the carbon monoxide emissions.

The data in table 2 and a visual inspection of figure 11 for CO show that there was not a statistically significant increase in CO with increasing iodine number.

NO_x

Figures 12 and 13 show the cold start and hot start data respectively for the oxides of nitrogen emissions. NO_x

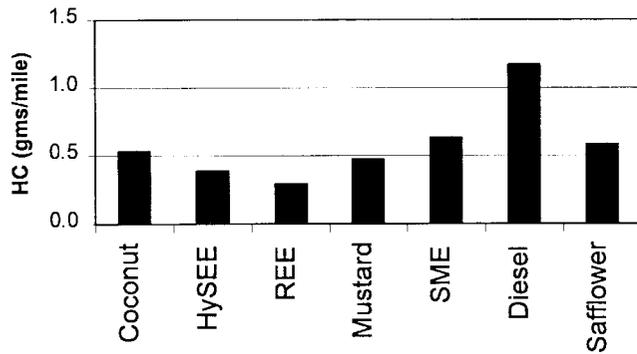


Figure 9–The HC for the six biodiesel feedstocks and diesel during the hot start emissions tests.

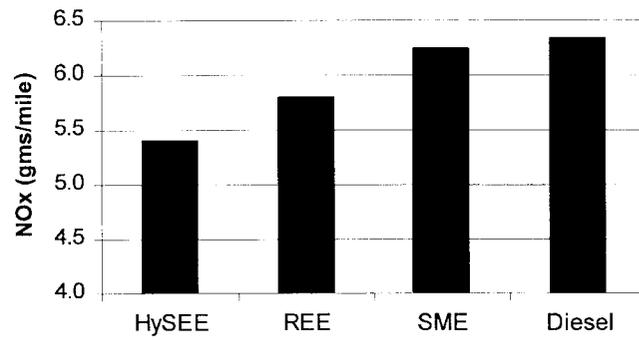


Figure 12–The NOx for the three biodiesel feedstocks and diesel during the cold start emissions tests.

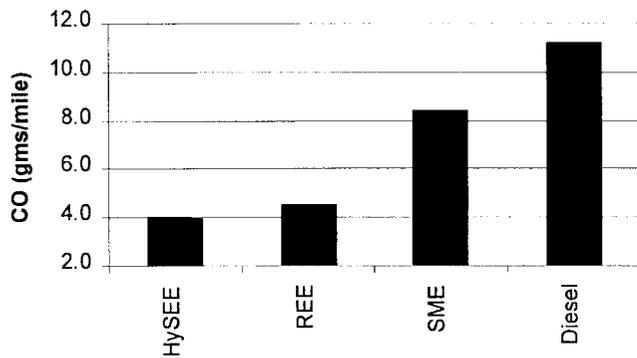


Figure 10–The CO for the three biodiesel feedstocks and diesel during the cold start emissions tests.

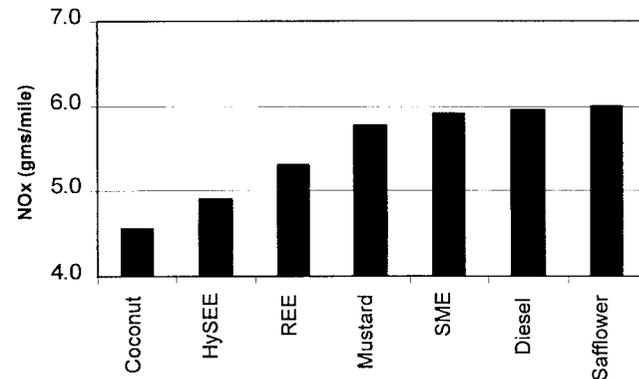


Figure 13–The NOx for the six biodiesel feedstocks and diesel during the hot start emissions tests.

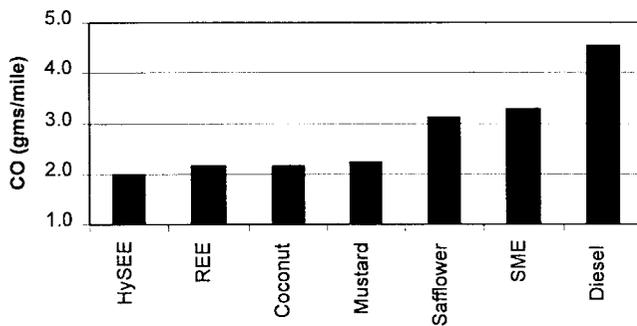


Figure 11–The CO for the six biodiesel feedstocks and diesel during the hot start emissions tests.

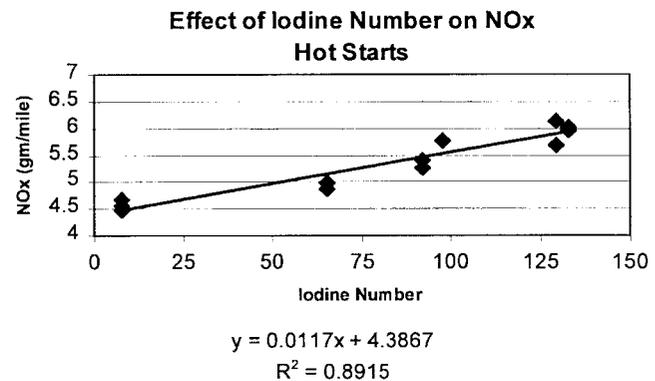


Figure 14–The NOx as a function of iodine number for the six biodiesel feedstocks during the hot start emissions tests.

increased with increasing iodine number. The linear equation, as shown in figure 14, resulted in an R^2 of 0.89 (hot starts only). The equation relating NO_x and iodine number was:

$$NO_x = 0.0117 \times \text{iodine number} + 4.387 \quad (1)$$

which shows that the NO_x increased 0.01 gm/mile for each 1 increase in iodine number of the biodiesel.

As figure 12 shows, the cold start NO_x data was affected very similarly to the hot starts, increasing NO_x with increasing iodine number. Insufficient data was available for statistical inferences.

PM

Figures 15 and 16 show the cold start and hot start data respectively for the particulate matter emissions. Regression analysis of the PM data versus iodine number resulted in fairly high R^2 values, 0.691 for the linear relationship but not so high as was seen for NO_x . The data in table 2 for PM shows that PM did not increase linearly with iodine number.

PM- NO_x COMPARISON

Diesel engines typically have a PM- NO_x trade-off, if one goes up the other goes down. Figure 17 shows PM versus NO_x for the cold start data and figure 18 PM versus NO_x data for the hot start tests. Clearly, the trade-off does

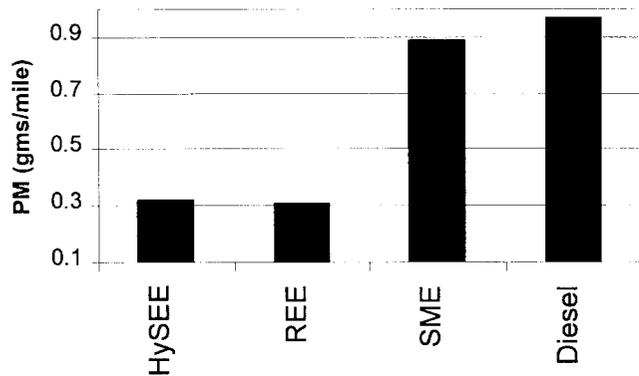


Figure 15—The PM for the three biodiesel feedstocks and diesel during the cold start emissions tests.

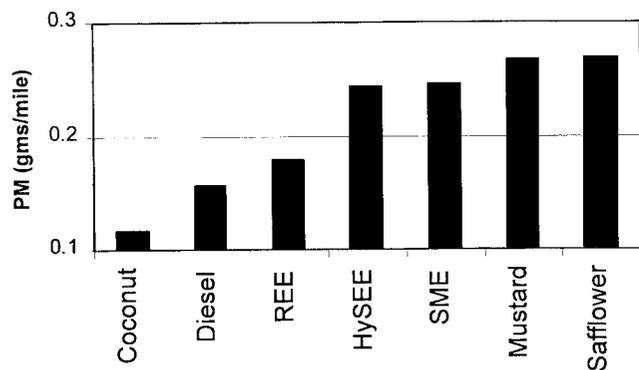


Figure 16—The PM for the six biodiesel feedstocks and diesel during the hot start emissions tests.

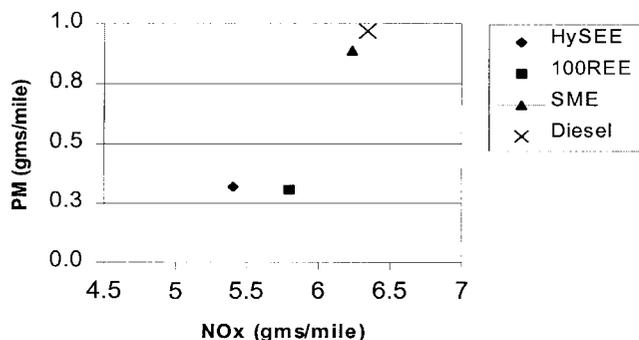


Figure 17—The PM-NOx comparison for the three biodiesel feedstocks and diesel during the cold start emissions tests.

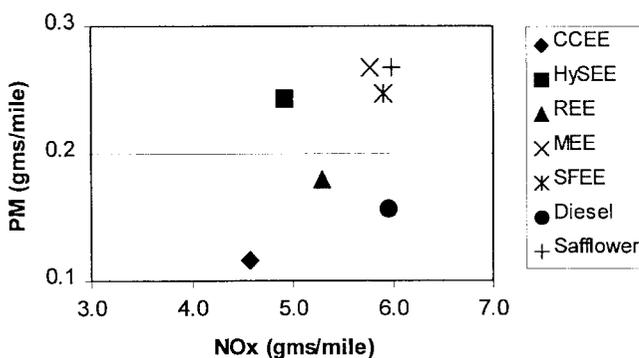


Figure 18—The PM-NOx comparison for the six biodiesel feedstocks and diesel during the hot start emissions tests.

not exist for the changes in NO_x resulting from changes in iodine number. When NO_x increased PM did not necessarily decrease, for example CCEE is low for both NO_x and PM and SFEE is high for both NO_x and PM compared to the other fuels. This suggests that the increase in NO_x due to a change in iodine number is not a simple effect on engine timing.

OTHER FUEL CHARACTERISTICS

This test was designed specifically to study the effect of iodine number on regulated emissions, however, since fuel characterization data was available for each of the fuels it was possible to examine the relationship between several other fuel characteristics and regulated emissions. However, the test was not designed for these other factors and thus the particular oils tested may not provide the widest possible range for the other characteristics.

Fuel characteristics assessed included total glycerol (TG); flash point (flash); pour point (pour); specific gravity (SG); molecular weight (MW); heat of combustion (HofC); cetane; weight percent of fatty acids with one double bond (one); weight percent of fatty acids with two double bonds (two); weight percent of fatty acids with three double bonds (three); combined one, two, and three (comb); and combined two and three (comb23). Each of these characteristics were statistically evaluated for R² values for HC, CO, NO_x, and PM for the hot start tests only. Table 6 provides R² values for the results of the regression analysis for these biodiesel fuel characteristics and HC, CO, NO_x, and PM for linear models. The R² values close to one indicate a good correlation.

Seven models had R² values above 0.8. Of these one was from the relationship of iodine number to NO_x which was already discussed. Five more had to do with the percentage of fatty acids with one, two or three double bonds in the biodiesel. The multiple regression considering two and three double bonds was more highly correlated with NO_x (R² = 0.889) than either the percentage of one

Table 6. The R² values for HC, CO, NO_x, and PM versus several biodiesel fuel characteristics LA MTA chassis dynamometer emissions tests for six biodiesel feedstocks

Fuel Characteristic	HC	CO	NO _x	PM
Iodine	0.044	0.490	0.892	0.691
Flash point	0.526	0.027	0.044	0.095
Pour point	0.090	0.013	0.107	0.000
SG	0.303	0.816	0.729	0.566
Cetane	0.256	0.268	0.517	0.508
Total glycerol	0.097	0.041	0.453	0.653
MW	0.350	0.009	0.256	0.274
Viscosity	0.594	0.122	0.055	0.154
Heat of comb	0.252	0.000	0.334	0.418
One double bond	0.646	0.273	0.047	0.047
Two double bonds	0.382	0.830	0.355	0.355
Three double bonds	0.108	0.001	0.040	0.040
One two three*	0.777	0.906	0.702	0.702
Two three*	0.434	0.843	0.889	0.448
Comb†	0.032	0.145	0.694	0.598
Comb23‡	0.334	0.843	0.730	0.403

* One, two, and three refer to the weight percent of fatty acids containing one, two, and three double bonds in the biodiesel feedstock.

† Comb refers to the combined percentage of of fatty acids containing one, two, and three double bonds in the feedstock.

‡ Comb23 refers to the combined percentage of fatty acids containing two and three double bonds in the feedstock.

double bond ($R^2 = 0.047$) or the percentage found by adding all one, two and three double bonds percentages (comb) ($R^2 = 0.694$) or by adding the two and three double bond percentages (comb23) ($R^2 = 0.730$). This data would suggest that the fatty acids with two double bond are important contributors to production of NO_x . Insufficient data exists in this data set to identify the contribution of three and higher double bonds.

The regression equations which were of interest by virtue of having high R^2 values, in addition to those for iodine number reported above, were:

$$NO_x = 0.0165 \times \text{comb23} + 4.884; R^2 = 0.730 \quad (2)$$

$$NO_x = 0.068 \times \text{three} + 0.0166 \times \text{two} + 4.672$$

$$R^2 = 0.889 \quad (3)$$

$$CO = 83.378 \times SG - 70.632; R^2 = 0.816 \quad (4)$$

$$CO = 0.016 \times \text{two} + 2.058; R^2 = 0.830 \quad (5)$$

$$CO = 0.165 \times \text{com23} + 1.983; R^2 = 0.843 \quad (6)$$

$$CO = 0.044 \times \text{three} + 0.014 \times \text{two} - 0.007$$

$$\times \text{one} + 2.232; R^2 = 0.906 \quad (7)$$

$$HC = 0.0099 \times \text{three} + 0.00094 \times \text{two}$$

$$- 0.0041 \times \text{one} + 0.578; R^2 = 0.777 \quad (8)$$

Double bonds were related to iodine number and also to NO_x production. Using comb23 (the sum of the percentage of two double bonds and three double bonds in each fuel) resulted in an R^2 of 0.92 and increased to only 0.94 when the percentage of one double bond was added. Evidently the higher order double bonds are increasingly important in producing undesirable NO_x .

An indication of the number of carbons in the fuel, MW was not highly correlated with emission levels. We can conclude that the number of double bonds is more important in predicting NO_x than is carbon chain length.

BLENDS

Figure 19 shows the 20% blends for each of the test fuels plotted versus NO_x , note that the same trend existed for increasing NO_x with increasing iodine number as with the neat fuels. The NO_x from the 20% blend of SME is

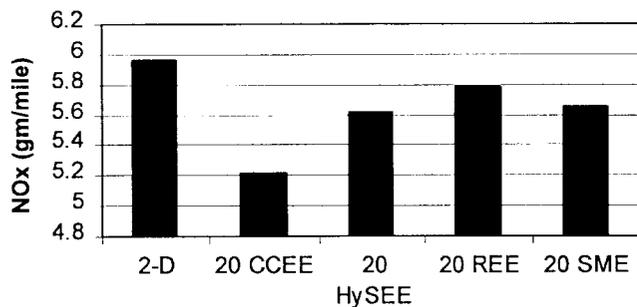


Figure 19–The NO_x emissions for the five biodiesel 20% blends and diesel measured during the hot start emissions tests.

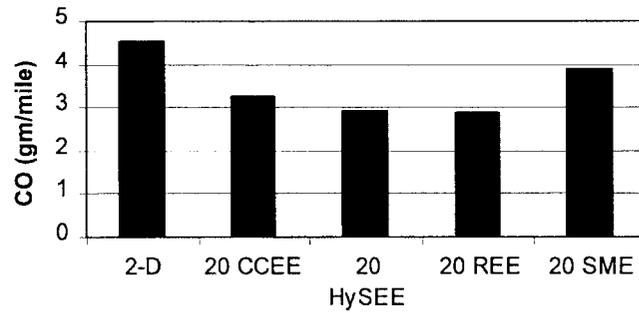


Figure 20–The CO emissions for the four biodiesel 20% blends and diesel measured during the hot start emissions tests.

8.6% higher than from CCEE, fairly close to 1/5 the value for the neat fuel showing the feedstock effect on NO_x is present in both the blends and for the neat fuels at about the ratio of the blend. The model for NO_x as a function of iodine number of the blends is given by the equation:

$$NO_x = 0.022 \times \text{iodine} + 5.182; R^2 = 0.646 \quad (9)$$

For each increase of iodine number by one in the blended fuel, NO_x increased by about 0.02 gm/mile. Diesel NO_x levels were higher than for the biodiesels, the NO_x levels for the blends are then between diesel and the neat biodiesels.

The other high regression coefficient for the blended fuels was for heat of combustion versus NO_x :

$$NO_x = 0.0023 \times \text{HofC} - 37.86; R^2 = 0.753$$

Figure 20 shows CO for the three 20% blends of biodiesel and diesel. Clearly the changes in CO are not a result of iodine number alone.

Since the other regulated emissions were not found to be affected by iodine number the results for the blended fuels for HC, CO, and PM are not shown.

CONCLUSIONS

These results demonstrate the effect feedstock can have on biodiesel characteristics and combustion. Developing triglycerides specifically for optimum use in biodiesel warrants additional study. Other specific conclusions of the study are:

1. Increasing iodine number of the biodiesel fuels used in this test was associated with increasing levels of NO_x for both hot start and cold start measurements.
2. The effect of iodine number of the biodiesel fuels on NO_x levels in the exhaust was still apparent in the 20% blends. A change in iodine number from 7.88 to 129.5 increased the NO_x by 29.3% in the neat fuels and 8.6% in the 20% blends.
3. A linear model fit the NO_x -iodine number data with an $R^2 = 0.892$.
4. Fatty acids with two double bonds appeared to have more effect on increasing NO_x emissions than did fatty acids with one double bond. Also, the number of double bonds had more effect on NO_x production than did carbon chain length.

5. Changes in PM due to biodiesel feedstock characteristics were not found to be highly correlated to iodine number.
6. Increasing iodine number of the biodiesel fuels used in this test did not affect the emission levels of HC, CO, CO₂ or PM in either hot start or cold start measurements.
7. In this study, small increases in total glycerol reduced the viscosity and heat of combustion.
8. Presence of double bonds in the fatty acids tend to increase viscosity, specific gravity, and heat of combustion.
9. Esterification was more difficult with lower carbon chain lengths as evidenced by a slight increase in total glycerol in the sample.

RECOMMENDATIONS

This study was designed to evaluate the effect of iodine number on regulated emissions. Data was also evaluated for the effect of several other fuel characteristics against these same emissions data. It would be appropriate to design tests specifically to determine in more detail some of these other effects, specifically molecular weight, cetane number, total glycerol, viscosity, and flash point. The fallibility of the present study in regard to these parameters is that the feedstocks were not selected for a range of these variables.

Based on the information gained from this and related studies, it may be possible to design the ideal triglyceride feedstock for biodiesel. A biodiesel with a combination of one or zero double bonds to minimize NO_x production and a low pour point to improve cold weather operation would have both environmental and climatic advantages. Plant breeders can thus alter the fatty acids of the feedstock to produce a triglyceride specifically for biodiesel.

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