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The production of isopropyl esters and their effects on a diesel engine

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The production of isopropyl esters and their effects on a diesel engine

by

Paul S. Wang

A thesis submitted to the graduate faculty
in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Major: Mechanical Engineering

Program of Study Committee:
Jon Van Gerpen, Major Professor
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Brent Shanks

Iowa State University

Ames, Iowa

2003

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Signatures have been redacted for privacy

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1. INTRODUCTION

The first use of vegetable oil in a compression ignition engine was first demonstrated through Rudolph Diesel who used peanut oil in his diesel engine [1]. The long term use of vegetable oils will lead to injector coking and the thickening of crankcase oil which leads to piston ring sticking [2-5]. Therefore, vegetable oils are not used in diesel engines because of endurance issues.

By transesterifying these vegetable oils, we get the alkyl monoesters of the fatty acids present in the vegetable oil. These esters are commonly referred to as biodiesel. Biodiesel is an alternative fuel that is renewable in the sense that its primary feedstock has a sustainable source. Some other feedstocks that can be converted to biodiesel are waste restaurant grease and animal fat. These sources are less expensive than vegetable oil.

In view of the current rise in oil prices, biodiesel is an attractive source of alternative energy. By increasing the use of biodiesel, the United States will also lessen its dependence on foreign oil reserves. The future of these oil reserves is also unknown in regards to the remaining amount of petroleum. While it is worthy to note that biodiesel will not completely displace petroleum diesel, biodiesel has its place as an alternative fuel and can be a source of lubricity as an additive to diesel fuel.

The emissions produced from biodiesel are cleaner compared to petroleum-based diesel fuel. Particulate emissions, soot, and carbon monoxide are lower since biodiesel is an oxygenated fuel. However, emissions of oxides of nitrogen (NO_x) are higher [6, 7] when biodiesel is used. The cause of the rise in NO_x is unknown and is being studied [8-10].

One particular problem of biodiesel is its cold flow properties. Neat biodiesel such as methyl soyate has a pour point (i.e. the lowest temperature at which the fuel is pourable) of -3°C [11]. In colder climates, crystallization can occur, which leads to the plugging of fuel filters and lines. Typically, in the U.S., biodiesel is blended with diesel fuel. A B20 blend would be 20% biodiesel in diesel fuel. Such a blend would have better cold flow properties compared to neat biodiesel. If neat biodiesel will be utilized solely and not blends, then steps need to be taken to improve the cold weather properties of biodiesel.

The scope of this research was to improve the cold weather properties of neat biodiesel by investigating the manufacture of isopropyl esters from soybean oil and yellow grease. Isopropyl esters have a lower crystallization temperature compared to methyl esters from the same source material. Table 1.1 shows the results from the research done by Lee [11], which compares the crystallization onset temperature for various fuels.

Table 1.1: Crystallization Onset Temperature for Various Fuels

Esters	Crystallization Onset Temperature ($^{\circ}\text{C}$)	
	Soybean Oil	Tallow
<i>Methyl</i>	5.2	17.8
<i>Isopropyl</i>	-6.0	6.6

The biodiesel made from tallow has a higher crystallization onset temperature because it has a higher amount of esters from saturated fatty acids. Table 1.2 compares the melting points for pure isopropyl and methyl esters from the prevalent saturated fatty acids in our feedstocks for this study, palmitic and stearic acid [12]. The data from Table 1.1 and 1.2 shows that methyl esters have higher crystallization temperature and melting points when

compared to their isopropyl ester counterparts. Thus, for better cold weather performance, isopropyl esters look very promising as a neat blend.

Table 1.2: Melting Point for Various Esters

Esters	Melting Point (°C)	
	C16:0 Hexadecanoic (Palmitic)	C18:0 Octadecanoic (Stearic)
<i>Methyl</i>	30	39.1
<i>Isopropyl</i>	13	28

Isopropyl esters have been successfully made in the past, but were expensive to produce. The goal was to reduce costs as much as possible while maintaining the quality of the fuel. Once the esterification process had been optimized to cut costs, enough fuel was produced at a pilot plant to facilitate engine testing. The fuel was tested in a John Deere¹ 4045TF engine to measure its performance characteristics and the emissions produced.

This thesis is divided into six sections; the introduction, literature review, procedure and test methods, analysis, results and discussion, and the conclusion.

¹ The mention of this company and other companies in this thesis does not imply endorsement or discrimination against other companies.

2. REVIEW OF LITERATURE

This chapter will review the work that has already been done with isopropyl esters. It will also provide background concerning fats and oils, transesterification, alcohols, and the cold flow properties of biodiesel.

Fats and oils are simple lipids that are hydrophobic substances and can be found in animals and plants. Fats and oils are also known as triacylglycerols, glycerides, or triglycerides because normally they consist of three fatty acids bonded together with glycerol. Generally, fats are solid at room temperature and oils are liquid at room temperature.

Fatty acids are long hydrocarbon chains that have a carboxyl group (COOH) at the end of the chain. Figure 2.1 below shows the structure for the carboxylic acid. A fatty acid can be denoted as CXX:Y, where XX represents the number of carbon atoms and Y represents the number of double bonds. A saturated fatty acid such as palmitic acid, C16:0 contains no double bonds and is more stable oxidatively (i.e. less reactive compared to oleic acid, which is unsaturated). Saturated fatty acids tend to occur more naturally in animal fats but can also be found in some vegetable oils such as palm oil.



Figure 2.1: Carboxylic Acid

Biodiesel is an oxygenated fuel that is produced by transesterifying triglycerides such as animal fats or vegetable oils with alcohol in the presence of a base or acid catalyst. Transesterification is the process of separating the fatty acids from their glycerol backbone to form fatty acid esters and free glycerol. Commonly, in the United States, biodiesel is

produced from soy bean oil reacted with methanol using a basic catalyst such as potassium hydroxide. This reaction will produce what are commonly known as soy oil methyl esters.

Figure 2.2 shows this reaction. R_1 , R_2 and R_3 can represent any fatty acid.

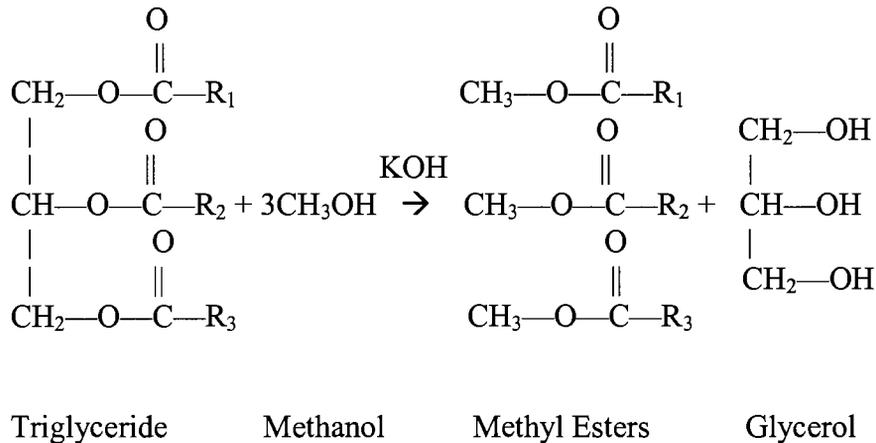


Figure 2.2: Transesterification of a Triglyceride Molecule with Methanol and Potassium Hydroxide to produce Methyl Esters and Glycerol

Producing biodiesel from sources that have a high percentage of saturated fatty acids will result in a fuel that is less prone to oxidation. However, the cold flow properties of the fuel will be affected since saturated fatty acids tend to have a higher melting point and are usually solid at room temperature. Although soy oil is composed mostly of unsaturated fatty acids, the methyl esters produced will still have cold flow problems below 0°C.

Crystallization occurs and the crystals from these esters will plug the fuel filters and lines.

The transesterification process can make use of other alcohols such as ethyl, butyl, and isopropyl alcohol. Methanol, ethanol and isopropanol are the most common alcohols with methanol having the highest demand followed by the other two. Among these alcohols, isopropanol is the only one with a branched structure. Figure 2.3 illustrates the reaction of a

triglyceride with isopropyl alcohol using potassium isopropoxide (KIP) as a catalyst to produce isopropyl esters.

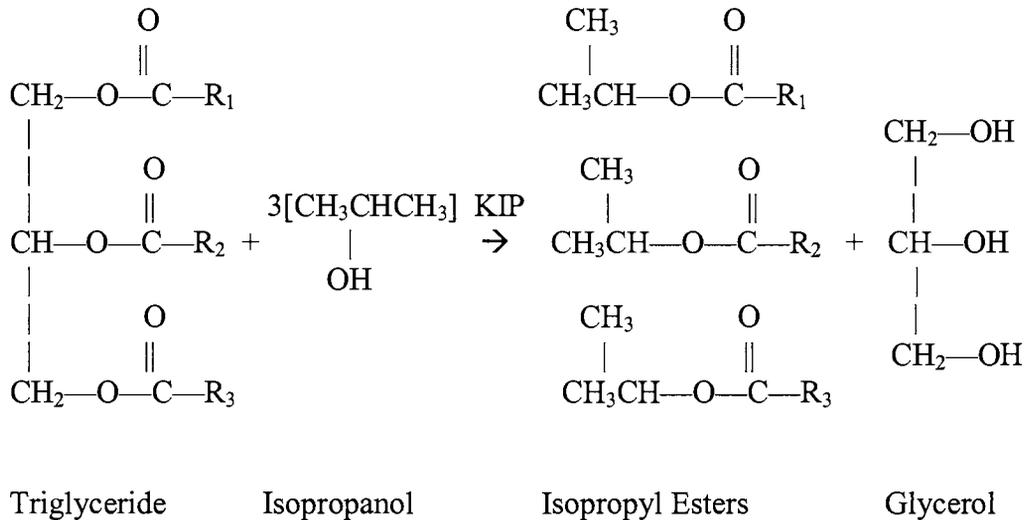


Figure 2.3: Transesterification of a Triglyceride Molecule with Isopropanol and Potassium Hydroxide to produce Isopropyl Esters and Glycerol

Lee et al. [11] researched the use of branch chain esters to reduce the crystallization temperature of biodiesel. In their study, they used branched chain alcohols such as isopropyl alcohol and 2-butyl alcohol to produce branch-chained esters. Using differential scanning calorimetry, they found that butyl esters and isopropyl esters crystallized at 12°-15°C and 7°-11°C lower, respectively, when compared to methyl esters of the same source material. Additionally, they compared the crystallization onset temperature of esters that were made from low palmitate soy oil and normal soy oil. The low palmitate soy isopropyl esters crystallized 5° – 6°C lower than the esters made from normal soy oil, indicating that biodiesel originating from a source material with less saturated fatty acids will have better cold flow properties. The low palmitate soy butyl esters had a pour point of -24°C, identical

to that of No. 2 diesel fuel. The cold flow properties of these branch-chained esters are further improved when blended with diesel fuel.

McCormick et al. [8] investigated the effects of biodiesel source material and chemical structure on emissions of criteria pollutants from a heavy duty engine. The molecular structure of the biodiesel was found to affect the emissions significantly. Further, it was found that fully saturated fatty acids with increasing chain length have lower NO_x emissions when compared with certification diesel. Additionally, NO_x emissions went up with lower cetane numbers and higher fuel density. Particulate matter (PM) was constant at about 0.07 g/bhp-h for all neat biodiesels as long as their density was less than 0.89 g/cm³ and the cetane number was greater than 45. In their study, they have also showed that density, cetane number, and iodine number correlated highly with one another. Their study also compared the emissions from ethyl esters and methyl esters and it was found that there was no significant difference in NO_x and PM emissions.

In another study, Wu and coworkers [13] tested low temperature properties for isopropyl esters made from tallow and ethyl esters from tallow and restaurant grease via lipase-catalyzed esterification. These fuels were blended with diesel (20:80, vol/vol) and their engine performance was evaluated. Isopropyl esters from tallow had better cold flow properties compared to ethyl esters from tallow. The crystallization onset temperature for isopropyl tallowate was 10.6°C compared to 17.8°C for ethyl tallowate. The cloud point, the temperature at which a cloud of crystals first appears under standard cooling conditions, was 9°C for isopropyl tallowate and 15°C for ethyl tallowate. Both esters had a pour point of 3°C. The isopropyl ester-diesel blend had physical and low temperature properties similar to No. 2 diesel fuel and the blend had similar engine performance.

3. EQUIPMENT, MATERIALS AND METHODS

This chapter will describe the equipment, material, and methods used in this research. The first part of this chapter will describe the experimental work performed in the laboratory to find a suitable recipe for producing isopropyl esters from soybean oil and yellow grease. The second part of this chapter will describe the mass production of the isopropyl ester at a pilot plant in Nevada. The facility in Nevada is known as the Biomass Energy Conversion (BECON) Center and is under the direction of the Iowa Energy Center. The third section will detail the engine runs and test schedule. Finally, the last section discusses the data acquisition and emissions equipment.

3.1 Optimizing the Transesterification Process for Isopropyl Esters

Producing isopropyl esters requires the use of isopropyl alcohol as opposed to methyl esters, which utilize methanol, or ethyl esters, which use ethanol. Commonly, most biodiesel consists of methyl esters and methanol is used since it is cheap and widely available. Methanol is priced between \$.04-.24/lb [14] and is the fourth largest organic chemical in the U.S. in terms of volume. Isopropanol, on the other hand, is priced between \$.20 - .34/lb [14], which makes it more expensive to make isopropyl esters. However, the yield for isopropyl esters is about 10% more than methyl esters because of the heavier molecular weight. So, this partially compensates for the increased cost.

Research done by Lee et al. [11] utilized isopropyl esters that were made from a 66:1 ratio of alcohol to triglycerides. The methyl esters produced at BECON uses a recipe that is a 6:1 molar ratio of methanol to triglycerides. The molecular weight of methanol is 32.04

and the molecular weight of isopropyl alcohol is 60.09. The heavier molecular weight compounded with the need for more moles of alcohol per mole of triglycerides increases the cost of producing isopropyl esters.

One of the first things to try was to vary the amount of isopropanol used and to examine the completeness of the transesterification process since the amount of alcohol used is the main reason for the higher cost of producing isopropyl esters. Three different molar ratios tried are shown in Table 3.1 below. The catalyst amount was varied to see how much was actually needed for each of these alcohol amounts. The completeness of the reaction is checked by doing the Total, Free and Combined Glycerol Iodometric-Periodic Acid Method (AOCS Official Method CA 14-56) [15]. The total glycerol is defined as the sum of free glycerol and the glycerol portion of any unreacted or partially reacted oil or fat [16]. Low levels of glycerol (<0.240 %) [16] means that a high conversion of triglycerides to mono-alkyl esters has taken place.

Table 3.1: Optimization Table for Manufacturing Isopropyl Esters

	Alcohol : Triglycerides	Catalyst Amount (% wt.)
Group 1	20:1	0.20, 0.33, 0.60, 1.00
Group 2	10:1	0.1, 0.28, 0.66, 1.1
Group 3	6:1	0.18, 0.68, 1.07

Table 3.1 shows the test matrix for finding the recipe that would save on cost but still produce quality biodiesel that meets the Standard Specification for Biodiesel Fuel (B100) Blend Stock for Distillate Fuels, ASTM D 6751-02 [16]. All the batches from Table 3.1 were made using fully refined soybean oil (Baker and Chefs) obtained from the local Sam's Club. The same amount of oil, 100 g, was used for every transesterification process. The catalyst amount on the third column of Table 3.1 was the weight of the sodium metal relative

to the weight of the oil. All the batches were transesterified with heat and were kept between 70 – 86 °C. To ensure no loss of alcohol, a reflux condenser was used. The setup is shown in Figure 3.1 below. All batches were reacted for at least eight hours. After the reaction, the contents from the reactor were placed in a separatory funnel. There was no separation of glycerol and biodiesel, and warm water (~60 °C) had to be added to aid the separation process. After several washes, clean biodiesel was obtained and its weight was measured to provide the yield.

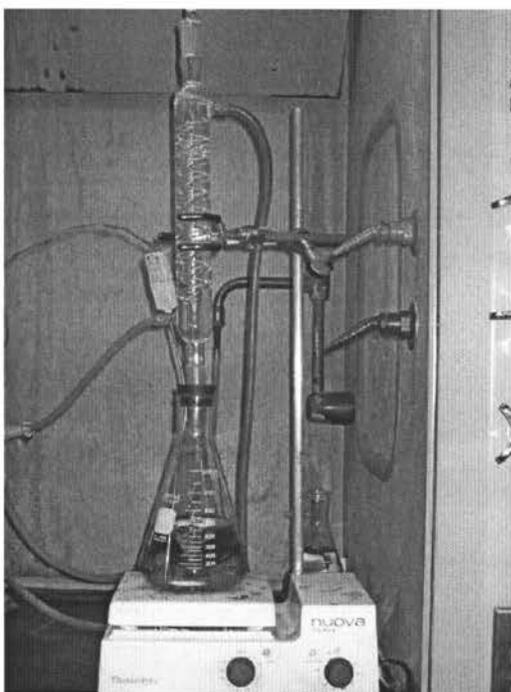
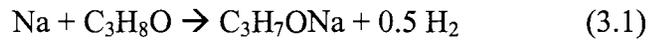


Figure 3.1: Small Reactor Setup

The research in the fuels laboratory utilized sodium isopropoxide as the catalyst. Sodium isopropoxide was manufactured in the laboratory by dissolving sodium metal in isopropyl alcohol. To speed up the slow reaction, the alcohol is agitated and heated on a stir plate. The isopropyl alcohol is heated to about 80 °C, just below the boiling point of 82.2 °C (at 760.00mm Hg). The chemical equation (3.1) for this reaction is given below:



However, making large quantities of sodium isopropoxide in the lab (for use in BECON) was risky and tedious. Hydrogen gas is released in this reaction, which is an explosion hazard. Making large quantities of catalyst was tedious because there was not any proper equipment to handle a large batch job. The reaction had to take place in a non-heated container and had to be purged with nitrogen. The solution was to purchase the catalyst from a chemical company. Since sodium isopropoxide was not readily available, potassium isopropoxide was purchased instead from Callery Chemical Company in Evans City, Pennsylvania.

Although potassium isopropoxide is a metal alkoxide like sodium isopropoxide, it will have a different reaction rate and reactivity on the transesterification process. Known amounts of potassium isopropoxide were tested to see how much catalyst was needed for the transesterification process. In the fuel lab, 10 ml and 20 ml of potassium isopropoxide (~20% wt.) in isopropanol was reacted with 100 g of soy oil to create two isopropyl ester samples. The isopropyl esters had a total glycerol number of 0.33% and 0.04% respectively. The amount of potassium metal present based on the weight of the triglyceride for the latter sample works out to be 1.34%. Due to the lack of time to fully optimize the amount of catalyst used, this setting that worked well was adopted in the mass production stage.

The other feedstock that was used for making isopropyl esters was yellow grease. The yellow grease was pretreated using the recipe from previous research done by Canakci et al. [17]. The recipe calls for a 20:1 molar ratio of methanol to free fatty acids and 5% sulfuric acid based on the weight of the free fatty acid material. This acid-catalyzed

pretreatment will convert these free fatty acids into methyl esters. Completing the biodiesel production with the base-catalyzed reaction will result in an isopropyl-methyl ester blend.

The acid-catalyzed pretreatment reaction was investigated by substituting methanol with isopropyl alcohol and even ethanol. However, isopropanol and ethanol were not as reactive as methanol and the pretreatment reaction could not reduce the free fatty acid material to the level required by the alkali-catalyzed reaction. Therefore, the fuels produced from the yellow grease in this study are actually blends of methyl and isopropyl esters (8.2%/91.8% wt.). Once the yellow grease has been pretreated, it was transesterified using the same recipe as found with the previous work using soybean oil.

3.2 Producing Isopropyl Esters in the Pilot Plant and Fuel Testing

The biodiesel pilot plant located at the Iowa Energy Center's Biomass Energy Conversion Center (BECON) in Nevada, Iowa, was utilized to mass produce isopropyl esters for engine testing. Soybean oil was pressed within the facility itself and yellow grease was obtained from National Byproducts in Des Moines, Iowa. The yellow grease had a free fatty acid content of 8.2 % and had to be pretreated with sulfuric acid and methanol. After pretreatment, the free fatty acid level was reduced to 0.86 %. Potassium isopropoxide in isopropyl alcohol (19.0 % weight) was obtained from Callery Chemical and isopropanol was obtained from Barsol Solvents, Des Moines. The transesterification followed a 20:1 molar ratio of alcohol to triglycerides and used 1.34% potassium by weight.

After producing the fuel, the glycerol test was done to see if it needed to be reacted again. Two samples of the fuel (one from yellow grease and the other from soy bean oil) were sent to Phoenix Chemical Laboratories in Chicago, IL to be tested for cetane number

and also for carbon and hydrogen content in the fuel itself. The grease that had been pretreated and the soy bean oil that were used to make the isopropyl esters were sent to Woodson – Tenent Laboratories in Des Moines for fatty acid profiling. These results will be presented in Chapter five. Other fuel properties such as specific gravity and viscosity were measured in the fuels lab in the Black Engineering Building at Iowa State University. The other fuels for engine testing were made at the BECON facility and the No. 2 diesel fuel was obtained from a commercial supplier.

3.3 Engine Setup and Test Schedule

The second part of this study was to examine the effects of isopropyl esters on a diesel engine with particular emphasis on the emissions. A John Deere 4045TF which is a four cylinder, four stroke, turbocharged diesel engine was utilized for this research. The basic information on this engine is presented in Table 3.2 below. The engine was coupled to a General Electric dynamometer (TLC 2544, direct current) rated at 112 kW. The original fuel pump on the 4045TF was replaced with another Stanadyne fuel pump when it suffered complete seizure. This failure was not caused by the use of biodiesel and occurred before the start of all testing described in this thesis. This other pump was sent to Des Moines Diesel to be adjusted to closely simulate the original pump operating characteristics.

Table 3.2: John Deere 4045TF Specifications

Bore	106.5 mm
Stroke	127 mm
Connecting Rod Length	203 mm
Compression Ratio	17.2
Maximum Power	67 kW @ 2200 rpm (intermittent)
Peak Torque	389 N-m @ 1400 rpm

To completely characterize the effects of isopropyl esters of soybean oil and yellow grease in a diesel engine, the testing also included No. 2 diesel fuel and methyl esters from soybean oil and yellow grease. The testing of the five fuels was conducted in random order and was repeated three times. Table 3.3 shows the engine testing schedule. All tests were conducted at an engine speed of 1400 rpm and engine torque was adjusted to 352.5 N-m for each run. This operating condition is 90% load for diesel fuel and close to full load for biodiesel. If the engine were operated at full load for all the different fuels, the torque values would be different because biodiesel has a lower heating value compared to No. 2 diesel fuel. Data was collected when the engine was at steady state operating conditions, when the engine oil temperature is stable.

The fuels were fed into the engine from five individual containers, one for each fuel. To ensure no contamination or mixing, the fuel lines were purged to remove the previous test fuel. The fuel was also thermally conditioned to be at 40°C.

Table 3.3: Engine Test Schedule for Five Different Fuels

<i>Repetition</i>	<i>Fuel Type</i>
First (352.5 N-m @ 1400 RPM)	No. 2 diesel fuel (DIE)
	Yellow Grease Methyl Esters (YGB)
	Soybean Oil Isopropyl Esters (ISBB)
	Soybean Oil Methyl Esters (SBB)
	Yellow Grease Isopropyl Esters (IYGB)
Second (352.5 N-m @ 1400 RPM)	Yellow Grease Methyl Esters (YGB)
	Soybean Oil Methyl Esters (SBB)
	Soybean Oil Isopropyl Esters (ISBB)
	Yellow Grease Isopropyl Esters (IYGB)
	No. 2 diesel fuel (DIE)
Third (352.5 N-m @ 1400 RPM)	Soybean Oil Isopropyl Esters (ISBB)
	No. 2 diesel fuel (DIE)
	Soybean Oil Methyl Esters (SBB)
	Yellow Grease Isopropyl Esters (IYGB)
	Yellow Grease Methyl Esters (YGB)

Fuel consumption was measured through the use of a stopwatch and an electronic mass balance. The fuel can was placed on the mass balance and when data were collected the stopwatch was started and the change in fuel weight was observed. Air consumption was measured by observing the pressure drop in laminar flow element. The calibration constant for the laminar element was given as $369.5 \text{ ft}^3/\text{min}/8'' \text{ H}_2\text{O}$ at 70°F and $29.92'' \text{ Hg}$.

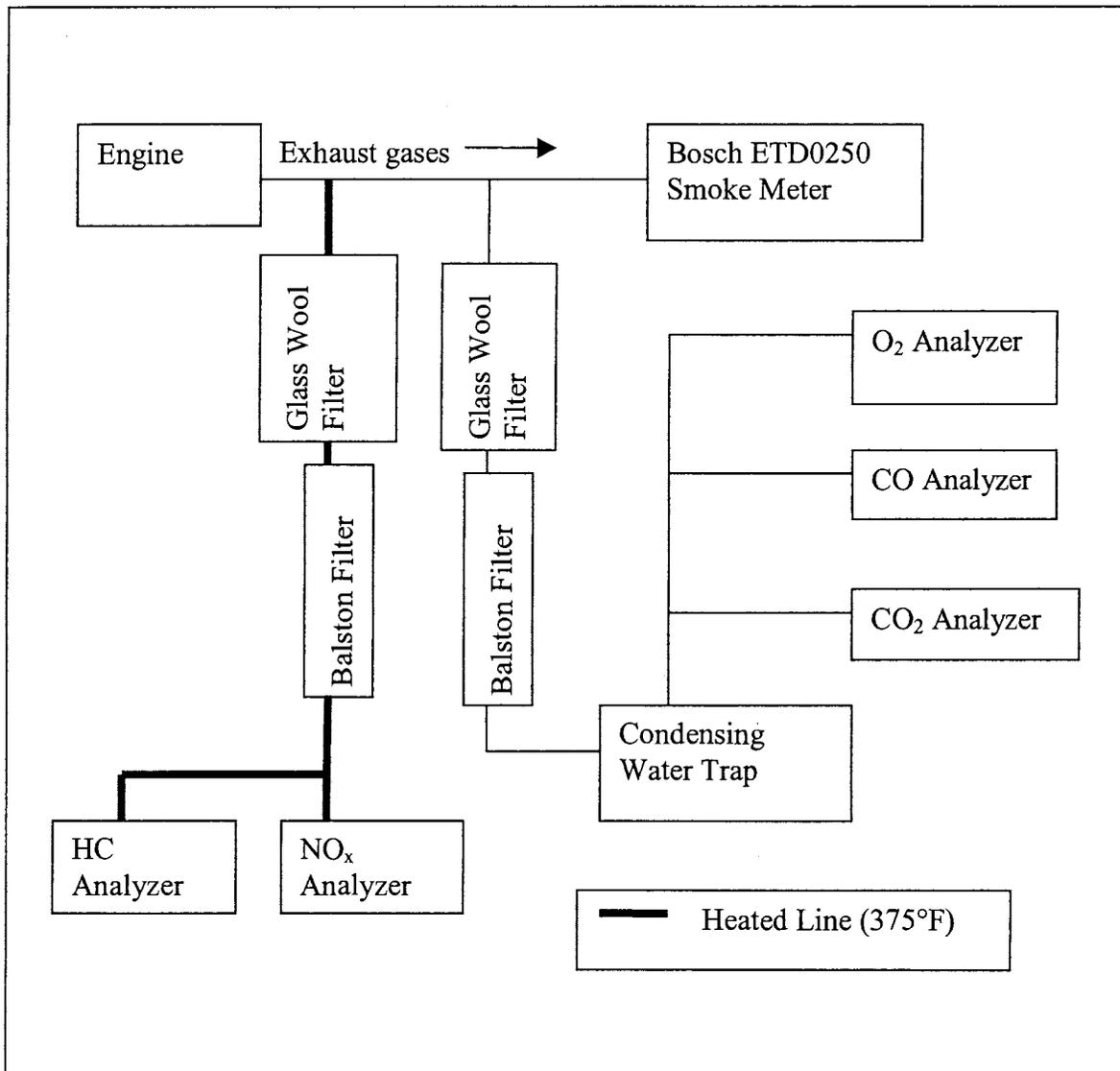
Other data that were recorded were engine oil pressure and turbocharger boost pressure. The dry and wet bulb temperatures were measured in the room where the intake air for the engine originated. Additionally, the temperatures for engine oil, intake manifold, inlet and outlet cooling water, inlet and outlet building water, and exhaust gases were also observed.

3.4 Data Acquisition and Emission Instruments

The schematic for the routing of the exhaust gases is shown in Figure 3.2. Each of the analyzers was calibrated individually and the calibration curves are given in the appendix. The results from the hydrocarbon analyzer and the NO_x analyzer were fed to a Pentium II PC using a National Instruments board and a Labview program. The results from the oxygen, carbon monoxide, and carbon dioxide analyzers were read directly from the instrumentation panel. To reduce error, these results were taken down twice, once when data acquisition started and at the end of the engine run for each fuel. Smoke numbers were obtained through the use of a Bosch ETD0250 smoke meter. The list of the analyzers used is given Table 3.4.

Table 3.4: Emission Analyzers

Analyzer	Model and Type
O ₂ monitor	Rosemount Analytical 755R
CO analyzer	Rosemount Analytical 880A non-dispersive infrared
CO ₂ analyzer	Rosemount Analytical 880A non-dispersive infrared
HC analyzer	J.U.M. Engineering VE7 flame ionization detector (FID)
NO/NO _x analyzer	Beckman Industrial 955 chemiluminescent

**Figure 3.2: Schematic of Exhaust Gas Routing**

4. DATA ANALYSIS

This chapter will describe the handling of the data collected from the emissions measurement part of this research. The calculation of the brake specific emissions and the correction for the oxides of nitrogen will be explained.

4.1 Gaseous Emissions

As mentioned in the previous chapter, the data collected include fuel consumption, air consumption, as well as the various gaseous emissions. The observed data was used in the calculation of the emissions produced from the engine. The emissions are reported on a brake specific basis (i.e. the mass flow rate of the pollutant divided by the engine power) to allow comparisons between different engines.

The general equation for the complete combustion of an oxygenated fuel is given in equation 4.1 below.



where

x = number of carbons in an average fuel molecule

y = number of hydrogens in an average fuel molecule

A/F = air-fuel ratio on a molar basis

B = moles of dry product gas per mole of fuel

y_i = mole fraction of chemical species on a dry basis

C = moles of water per mole of fuel

By accounting for the atom balances and knowing the air-fuel ratio from the fuel and air consumption measurements, B and C are expressed as follows:

$$B = (A/F) + z/2 - y/4 \quad (4.2)$$

$$C = y/2 \quad (4.3)$$

The observed emission data were then processed to be reported on a brake specific basis. The following equations are the brake specific equation for the various species observed.

$$\begin{aligned} BSCO_2 &= [\text{kmol CO}_2/\text{kmol dpg}] \times [\text{kmol dpg}/\text{kmol fuel}] \times [\text{kmol fuel}/\text{kg fuel}] \\ &\quad \times [\text{kg fuel}/\text{hr}] \times [\text{kg CO}_2/\text{kmol CO}_2] \times [1/\text{kW}] \quad (4.4) \\ &= [y_{CO_2}] \times [B] \times [MW_{fuel}] \times [m_{fuel}] \times [MW_{CO_2}] \times [1/\text{kW}] \\ &= \text{kg/kW-h} \end{aligned}$$

The first term, y_{CO_2} , is the mole fraction of carbon dioxide from the dry product gas. As defined in equation 4.2, B is the moles of dry product gas per mole of fuel. Both of these terms are multiplied out with the mass flow rate of the fuel, fuel molecular weight and then divided by the engine power. The units will work out to give kg/kW-h. Similarly, the other pollutants are handled in the same manner and their equations are listed below. Note that the NO and HC analyzers measure the pollutants on a wet basis and when accounting for this, the sum of equations 4.2 and 4.3 (B + C) is used to represent the moles of wet product gas per mole of fuel.

$$\begin{aligned} BSCO &= [\text{kmol CO}/\text{kmol dpg}] \times [\text{kmol dpg}/\text{kmol fuel}] \times [\text{kmol fuel}/\text{kg fuel}] \\ &\quad \times [\text{kg fuel}/\text{hr}] \times [\text{kg CO}/\text{kmol CO}] \times [1/\text{kW}] \quad (4.5) \end{aligned}$$

$$\begin{aligned} BSNO_x &= [\text{kmol NO}_x/\text{kmol wpg}] \times [\text{kmol wpg}/\text{kmol fuel}] \times [\text{kmol fuel}/\text{kg fuel}] \\ &\quad \times [\text{kg fuel}/\text{hr}] \times [\text{kg NO}_x/\text{kmol NO}_x] \times [1/\text{kW}] \quad (4.6) \end{aligned}$$

$$\begin{aligned} BSHC &= [\text{kmol HC}/\text{kmol wpg}] \times [\text{kmol wpg}/\text{kmol fuel}] \times [\text{kmol fuel}/\text{kg fuel}] \\ &\quad \times [\text{kg fuel}/\text{hr}] \times [\text{kg HC}/\text{kmol HC}] \times [1/\text{kW}] \quad (4.7) \end{aligned}$$

where

dpg = dry product gas

wpg = wet product gas

MW = molecular weight

m_{fuel} = mass flow rate of fuel (kg/hr)

kW = brake power (kW)

4.2 Humidity Correction Factor for Oxides for Nitrogen

The humidity correction for the oxides of nitrogen, as prescribed by the Society of Automotive Engineers (SAE) [18], is given by equation 4.8.

$$\text{NO}_{\text{corr}} = \text{NO}_{\text{wet}} \times 1/K \quad (4.8)$$

Where

NO_{corr} = corrected NO concentration, ppm

NO_{wet} = observed NO concentration on a wet basis, ppm

$$K = 1 + 7A (h - 10.714) + 1.8B (T - 29.444)$$

$$A = 0.044 (F/A) - 0.0038$$

$$B = -0.116 (F/A) + 0.0053$$

T = intake air temperature, °C

F/A = fuel-air ratio (dry basis)

h = specific humidity, g H₂O/kg dry air

The specific humidity, h can be calculated from the following equation.

$$h = 621.10 \times P_v / (P_b - P_v) \quad (4.9)$$

where

P_v = partial pressure of water vapor, kPa

P_b = measured barometric pressure, kPa

To calculate the partial pressure of the water vapor, we employ Ferrel's equation [19] as shown below.

$$P_v = P_w - 1.80A \times P_b (T_d - T_w) \quad (4.10)$$

where

P_w = saturation pressure of water vapor at the wet bulb temperature, kPa

$A = 3.67 \times 10^{-4} (1 + 0.001152 T_w)$, an experimentally derived constant

T_d = dry bulb temperature, °C

T_w = wet bulb temperature, °C

The saturation pressure of water vapor at the wet bulb temperature is obtained through a least square fit to data from Keenan and Keye's steam table [20], shown by equation 4.11.

$$P_w = 0.6048346 + 4.59058 \times 10^{-2} \times T_w + 1.2444 \times 10^{-3} \times T_w^2 + 3.52248 \times 10^{-5} \times T_w^3 + 9.32206 \times 10^{-8} \times T_w^4 + 4.18128 \times 10^{-9} \times T_w^5 \quad (4.11)$$

5. RESULTS AND DISCUSSION

This chapter is divided into two parts. The first part presents and describes the results observed from the production of isopropyl esters in the fuels laboratory. The other section details the results obtained from engine testing.

5.1 The Manufacture of Isopropyl Esters

As described in chapter three, three different ratios of isopropyl alcohol to triglycerides was used in this study, 6:1, 10:1, 20:1. At each molar ratio setting, different levels of sodium metal were used. The response variable is the total glycerol number, which indicates whether the reaction was complete or not complete. Table 5.1 below indicates the total glycerol value for each of the different combinations of catalyst and alcohol amount. Figure 5.1 is the graphical representation for the values in Table 5.1.

Table 5.1: Total Glycerol Value for Three Different Isopropanol Molar Ratios and Varying Amounts of Sodium Metal

6:1 Molar ratio		10:1 Molar ratio		20:1 Molar ratio	
(% wt.) sodium	Total Glycerol (% wt.)	(% wt.) sodium	Total Glycerol (% wt.)	(% wt.) sodium	Total Glycerol (% wt.)
0.18	8	0.1	2.4	0.1	1.18
0.68	2.22	0.28	1.6	0.33	0.922
1.07	0.85	0.66	1.1	0.6	0.724
N/A	N/A	1.1	0.8	1	0.176

From Figure 5.1, it is obvious that the best combination for to use to get a quality fuel is a 20:1 alcohol to triglyceride ratio and one percent sodium metal by weight with respect to the triglycerides.

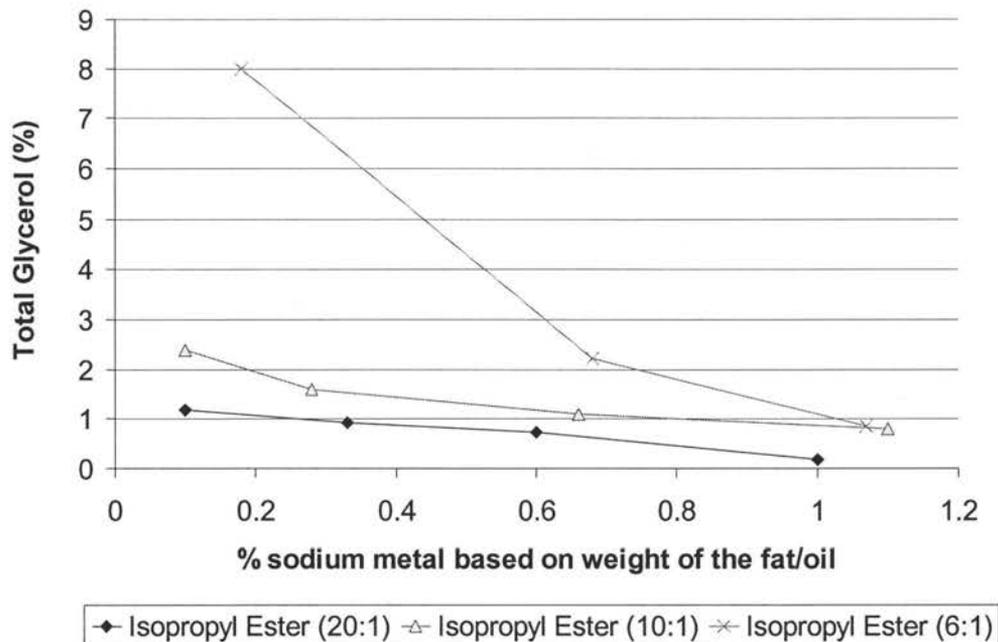


Figure 5.1: Total Glycerol vs. Amount of Sodium Metal (% weight)

The next step of this research investigated the possibility of using isopropyl alcohol for the acid pretreatment of yellow grease. Ethanol was also used as a comparison. All reactions used a 20:1 molar ratio of alcohol to free fatty acids and five percent sulfuric acid. The base material was yellow grease with a free fatty acid content of 13%. Figure 5.2 depicts how the acid value changed with time. Based on Figure 5.2, methanol has the best reactivity followed by ethanol and isopropyl alcohol is least effective in pretreating the yellow grease. With these results, isopropyl esters from yellow grease were developed via pretreatment using 5 % sulfuric acid and a 20:1 methanol to triglycerides ratio. Once the free

fatty acid content had dropped below 1%, the rest of the material was reacted using a 20:1 isopropyl alcohol to triglycerides ratio with 1% sodium metal.

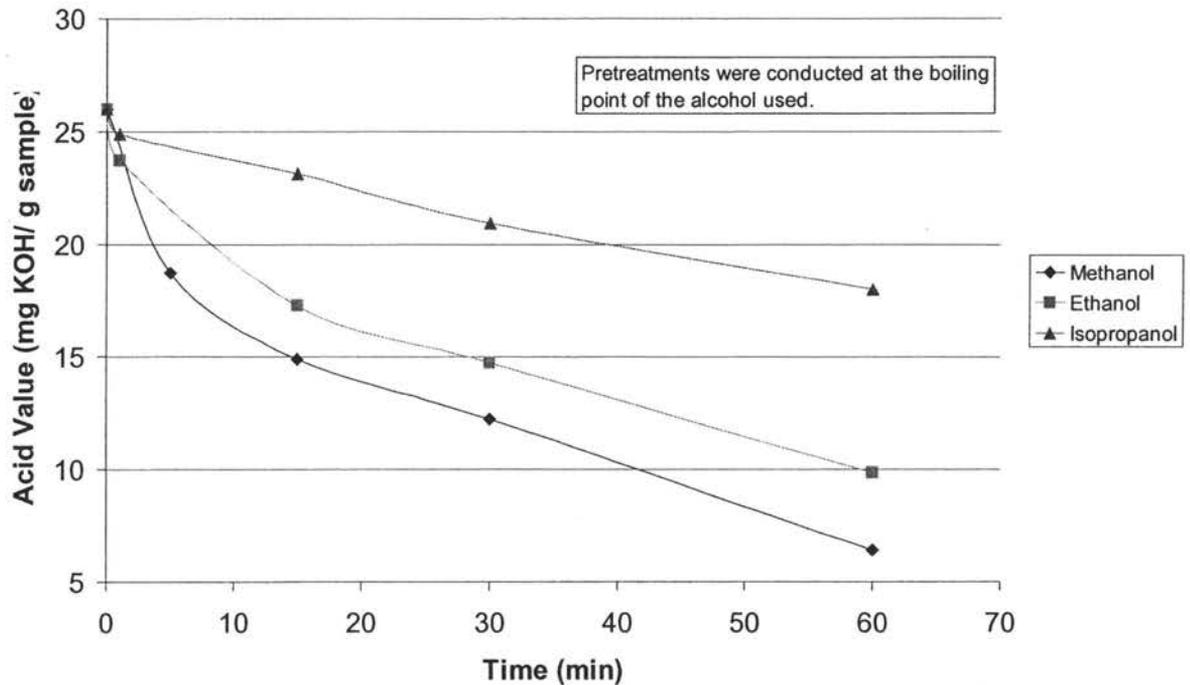


Figure 5.2: Comparison of Pretreatments using Different Alcohols

The physical properties and composition for the fuels used in engine testing are presented in Table 5.2. The free fatty acid profiles for the source material of the four biodiesels are shown in Table 5.3.

Table 5.2: Fuel Properties

Test Property	No 2 diesel fuel	Soybean Oil Methyl Ester	Yellow Grease Methyl Ester	Soybean Oil Isopropyl Ester	Yellow Grease Isopropyl Ester
Carbon (% mass) ^d	86.66 ^a	77.00	76.66	77.90	77.40
Hydrogen (% mass) ^d	12.98 ^a	12.18	12.33	12.13	12.49
Oxygen (% mass) ^d	-	10.82	11.01	9.97	10.11
C/H Ratio	6.676	6.322	6.217	6.422	6.197
Sulfur (% mass) ^a	0.034	<0.005	<0.005	<0.005	<0.005
Typical Formula	C _{14.01} H _{25.00} ^b	C _{18.74} H _{34.51} O ₂ ^d	C _{18.40} H _{35.26} O ₂ ^d	C _{20.76} H _{38.53} O ₂ ^d	C _{20.27} H _{38.99} O ₂ ^d
Average Molecular Weight	194.14 ^b	291.73 ^d	288.29 ^d	320.14 ^d	314.53 ^d
Cetane Number (ASTM D613) ^a	42.2	50.4	62.6	51.5	65.6
Hydrocarbon Type, FIA (ASTM D1319) ^a					
Saturates	56.6	-	-	-	-
Olefins	1.6	-	-	-	-
Aromatics	41.8	-	-	-	-
Gross Heat of Combustion (Btu/lb) ^a	19419	17183	17252	17324	17367
Net Heat of Combustion (Btu/lb) ^a	18235	16072	16209	16155	16239
Specific Gravity ^c	0.8559	0.8796	0.8722	0.8704	0.8617
Kinematic Viscosity (@40°C, mm ² /s) ^c	2.8911	4.5926	5.9156	5.2649	6.0997
Total Glycerol (%) ^c	-	0.175	0.194	0.227	0.082

^aMeasured by Phoenix Chemical Laboratory Inc., Chicago, IL^bCalculated using UOP Method 375-86^cMeasured at the Mechanical Engineering Department, Iowa State University^dCalculated from Fatty Acid Profile unless stated otherwise

Table 5.3: Fatty Acid Profiles for the Engine Test Fuels

Fatty Acid Profile	SBB	YGB	ISBB	IYGB
C14:0 Tetradecanoic (Myristic)	<0.10	1.27	<0.10	1.25
C14:1 Tetradecenoic (Myristoleic)	<0.10	0.43	<0.10	0.39
C15:0 Pentadecanoic	<0.10	0.18	<0.10	0.17
C16:0 Hexadecanoic (Palmitic)	10.81	17.44	11.07	17.08
C16:1 Hexadecenoic (Palmitoleic)	0.11	2.03	<0.10	2.01
C17:0 Heptadecanoic (Margaric)	<0.10	0.51	0.1	0.46
C17:1 Heptadecenoic (Margaroleic)	<0.10	0.41	<0.10	0.4
C18:0 Octadecanoic (Stearic)	4.54	12.38	4.45	11.4
C18:1 Octadecenoic (Oleic)	24.96	54.67	24.13	56.82
C18:2 Octadecadienoic (Linoleic)	50.66	7.96	51.53	7.69
C18:3 Octadecatrienoic (Linolenic)	7.27	0.69	7.41	0.56
C18:4 Octadecatetraenoic	<0.10	0.13	<0.10	0
C20:0 Eicosanoic (Arachidic)	0.37	0.25	0.35	0.24
C20:1 Eicosenoic (Gadoleic)	0.32	0.52	0.23	0.55
C20:2 Eicosadienoic	<0.10	0.11	<0.10	0.13
C22:0 Docosanoic (Behenic)	0.42	0.21	0.39	0.21
C24:0 Tetracosanoic (Lignoceric)	0.12	0	0.11	0
Unknown	0.32	0.81	0.23	0.64

SBB: Soybean Oil Methyl Ester

YGB: Yellow Grease Methyl Ester

ISBB: Soybean Oil Isopropyl Ester

IYGB: Yellow Grease Isopropyl Ester

5.2 Engine Emissions Results

This section will discuss the results from the engine emissions tests. The engine emissions that are reported here are on a brake specific basis (g/kW-h) for an operating condition of 352.5 N-m and 1400 rpm. All fuels were run at this operating condition, which means that the brake power was constant. The measured emissions are carbon monoxide (CO), carbon dioxide (CO₂), unburned hydrocarbons (HC), oxides of nitrogen (NO_x), and the Bosch Smoke Number. Since only three data points were taken for each fuel, the error bars on the charts represent the highest and lowest datum recorded. The bar represents the average of the three values of the brake specific emissions for each fuel.

The objective for the engine testing was to observe if there were any differences between the pollutants from the combustion of the four types of biodiesels and the No. 2 diesel fuel. The other objective was to investigate for any differences between the isopropyl esters and methyl esters from the same source material. To answer these questions, an Analysis of Variance (ANOVA) was done to see if at least two of the means are not equal. (The ANOVA tables are presented in the Appendix.) This was followed by a statistical analysis called the Tukey Method, which was used to check if there was any significant difference between the means of all possible pairs. In the tables that follow, fuels that are not connected by the same letter/letters are significantly different. The error rate of $\alpha = 0.05$ applies to the family of all paired comparisons, which corresponds to a 95% confidence level. A summary of all results will be presented first to give the reader an overview, followed by detailed discussion of the individual pollutants with the Tukey groupings.

5.2.1 Overview of Emissions Results

The baseline fuel for comparison in emissions here is No. 2 diesel fuel. Table 5.6 below shows the percent change in emissions relative to No. 2 diesel fuel and Figure 5.3 is the graphical representation of the tabular data.

Table 5.6: Percent Change in Emissions relative to No. 2 diesel fuel

	CO	CO ₂	HC	NO _x	Smoke
SBB	-33.67	-0.13	-49.94	10.25	-43.57
YGB	-27.19	-1.02	-53.31	-1.71	-39.42
ISBB	-10.28	0.04	-44.41	5.37	-37.76
IYGB	-18.49	-0.77	-42.91	-2.73	-36.93

From Table 5.6 it is noted that there are obvious reductions of carbon monoxide, hydrocarbons, and smoke numbers for all four biodiesel fuels. The reduction that occurred ranged from 10.3% to 33.7%, 42.9% to 53.3% and 36.9% to 43.6% for CO, HC and smoke numbers respectively. The change for carbon dioxide emissions was very small and the results are mixed for the oxides of nitrogen. The combustion of biodiesel originating from soybean oil has higher oxides of nitrogen compared to No. 2 diesel fuel and is higher for soy oil methyl esters (10.25 % increase) compared to soy oil isopropyl esters, which saw a 5.37% increase. There was a slight reduction in oxides of nitrogen for the yellow grease-based biodiesel, which saw a 1.7% to 2.7% decrease. There seems to be some similarities for biodiesels originating from the same source material. By using the Tukey grouping, the means for the methyl and isopropyl esters originating from the same source material will be compared to see if there is any significant difference.

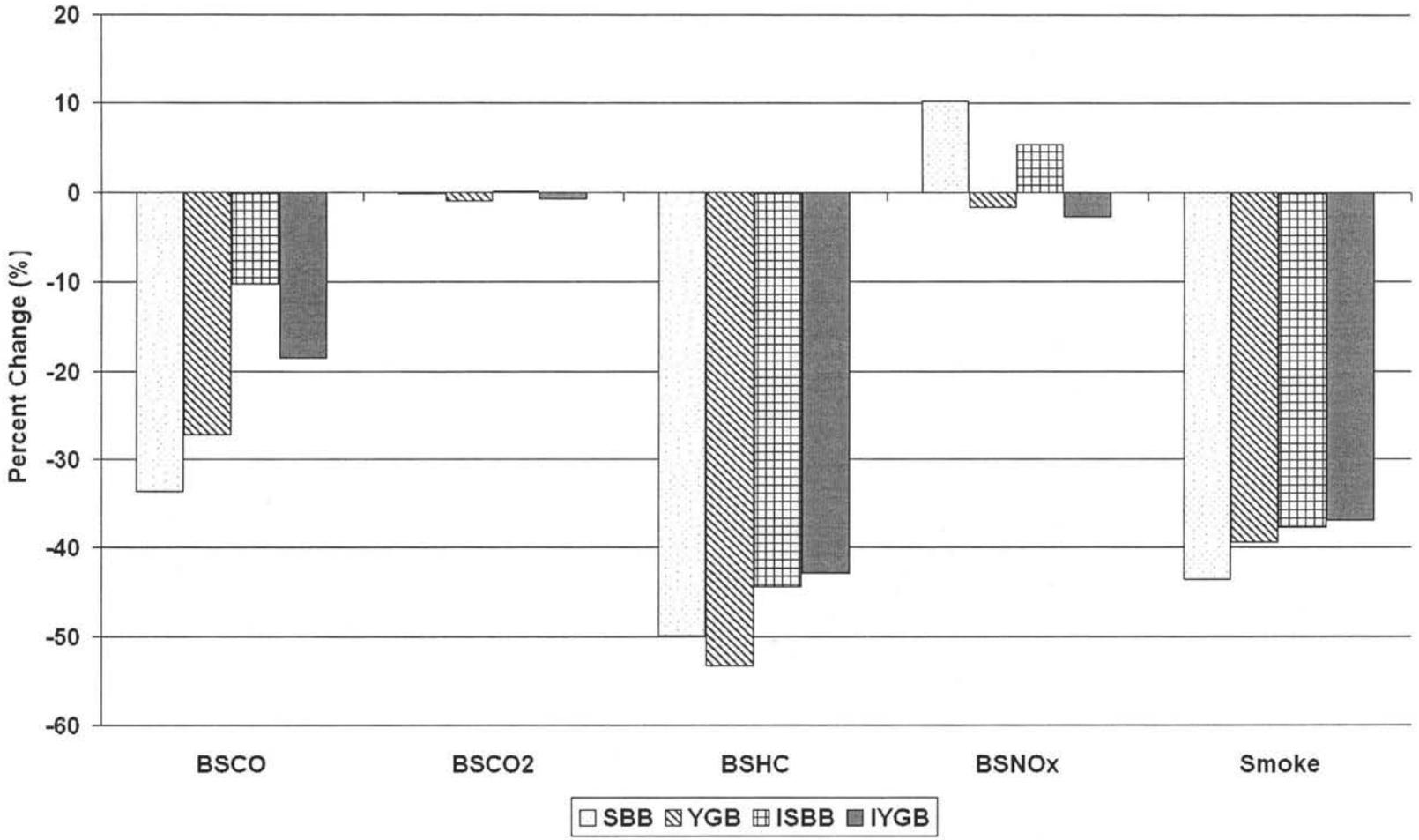


Figure 5.3: Percent Change in Emissions relative to No. 2 diesel fuel

5.2.2 Carbon Monoxide (CO) Emissions

Figure 5.4 shows the brake specific carbon monoxide (g/kW-h) for all five fuels. Three replications were done for each fuel as shown. The plot was generated using JMP, a statistical software package. The vertical spans of the diamonds represent the 95% confidence level for each group and the horizontal line in the middle of the diamond is the group mean. The spans for the five diamonds are the same because the mean square error was used in the determination of this confidence level. The angle of intersection for the any two circles on the right represents the level of significance. For clarity, refer to Figure 5.5. If the angle of intersection is greater than 90° , such as that shown in the first pair of circles, then the means are not significantly different. The means are significantly different when the angle of intersection is less than 90° such as the third pair of circles.

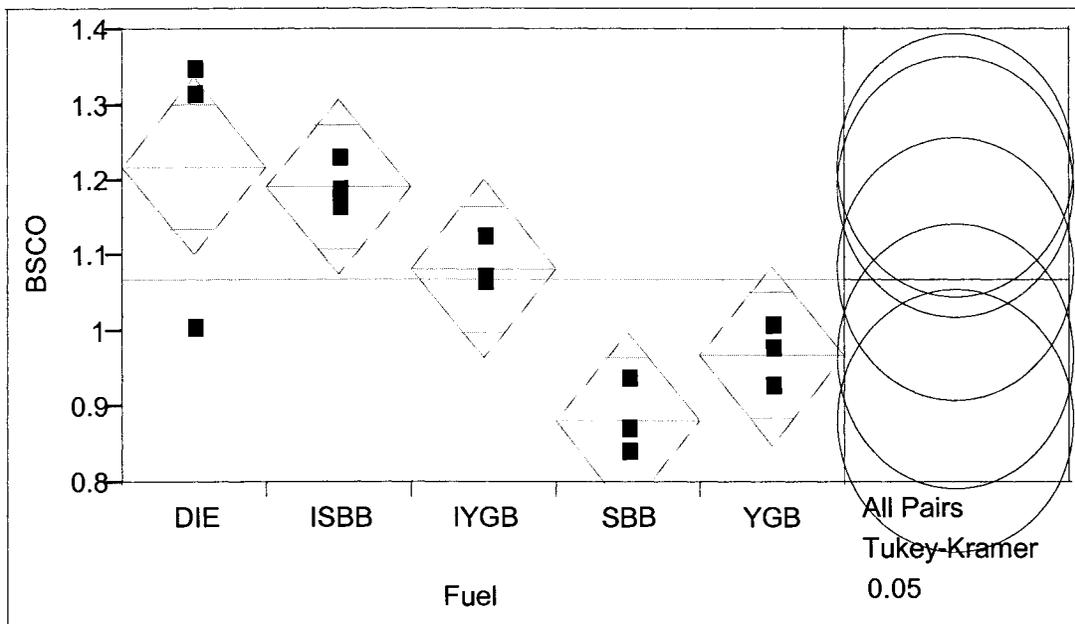


Figure 5.4: Carbon Monoxide Emissions for Various Fuels.

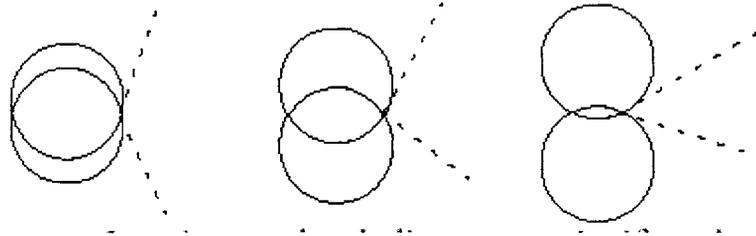


Figure 5.5: Angle of Intersection

From Figure 5.4, it appears that one of the carbon monoxide emissions for diesel is an outlier. All of the other results were within the 95% confidence interval and it seems like the lowest data point for the diesel run is inconsistent with the rest of the CO data collected. Referring back to the raw data where the internal scale reading was taken from the CO analyzer, that data point was registered at 14.8% while the other two read 19.5% and 19.05%. Clearly, this point was off and was not noticed since it was the very first reading in all of the runs. This was probably an error in the CO analyzer since all the other data taken for the DIE 1 run were fine. To make better sense of the data, this outlier was excluded from the statistical analysis on the CO emission.

Figure 5.6 represents the means of the CO emission for the various fuels. From the Tukey grouping in Table 5.7, the mean for No. 2 diesel fuel is significantly different from the rest of the biodiesels. Additionally, the means of isopropyl esters and methyl esters from the same source material are significantly different whereas methyl esters from soy bean oil and yellow grease are not significantly different.

All four biodiesels exhibited a reduction in CO emissions compared to the baseline fuel with soybean methyl esters having the largest drop by 33.7%. Isopropyl esters from soybean oil had the least reduction with a 10.3% drop. Consistent with previous findings [6, 7], the CO emissions are lower for biodiesel when compared to the baseline fuel which has the highest CO emissions. Canakci [7] found the CO emissions for soy methyl esters and yellow grease methyl esters to be 18.2% and 17.8% lower compared to diesel. Monyem [6] found a 15.7% and 15.8% drop for the same fuels when compared to No. 2 diesel fuel. However, it must be noted that the isopropyl esters had higher CO emissions compared to the methyl esters and this difference was significant. On the other hand, the CO emissions for both types of methyl esters were not significantly different from each other.

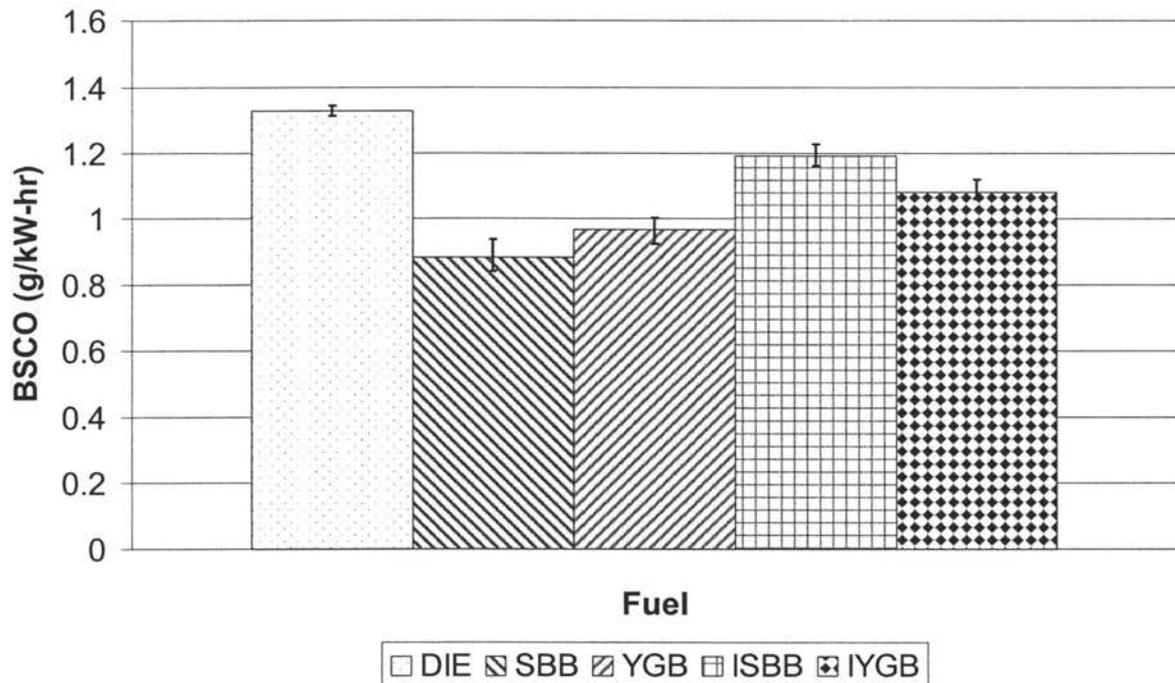


Figure 5.6: Brake Specific CO Emissions at 352.5 N-m and 1400 rpm

Table 5.7: Tukey Grouping for BSCO

Level		Mean (g/kW-h)
DIE	A	1.328
ISBB	B	1.192
IYGB	C	1.083
YGB	D	0.967
SBB	D	0.881

5.2.3 Carbon Dioxide (CO₂) Emissions

Figure 5.7 shows the means for the brake specific CO₂ emissions for each of the five fuels at 352.5 N-m and 1400 rpm. According to the Tukey grouping, the means are not significantly different statistically.

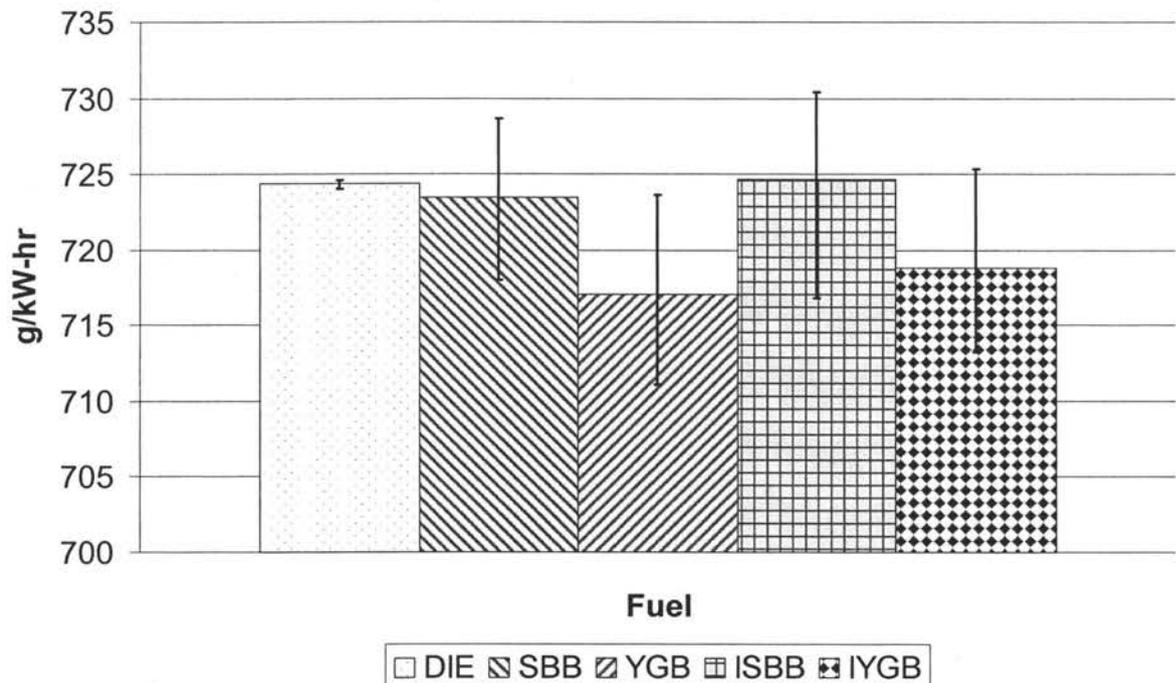


Figure 5.7: Brake Specific CO₂ at 352.5 N-m and 1400 rpm

When comparing to the baseline fuel, the CO₂ emissions do not change much, consistent with previous research [6, 7]. Methyl esters from grease had the biggest reduction in CO₂ and that represents only a 1.02% drop, which is not much, and the CO₂ emissions from the soy oil isopropyl esters were nearly identical to No. 2 diesel fuel.

Table 5.8: Tukey Grouping for BSCO₂

<i>Level</i>	<i>Mean (g/kW-h)</i>
ISBB A	724.69
DIE A	724.42
SBB A	723.49
IYGB A	718.81
YGB A	716.99

5.2.4 Unburned Hydrocarbon (HC) Emissions

All four biodiesels showed significant reductions in unburned hydrocarbons when compared to No. 2 diesel fuel. According to the Tukey grouping in Table 5.9, all four types of biodiesel are significantly different from No. 2 diesel fuel. However, the four biodiesels are not significantly different from each other.

Table 5.9: Tukey Grouping for BSHC

<i>Level</i>	<i>Mean (g/kW-h)</i>
DIE A	0.1486
IYGB B	0.08483
ISBB B	0.08259
SBB B	0.07437
YGB B	0.06937

Figure 5.8 below shows the means of the unburned hydrocarbon emissions for the various fuels at 352.5 N-m and 1400 rpm.

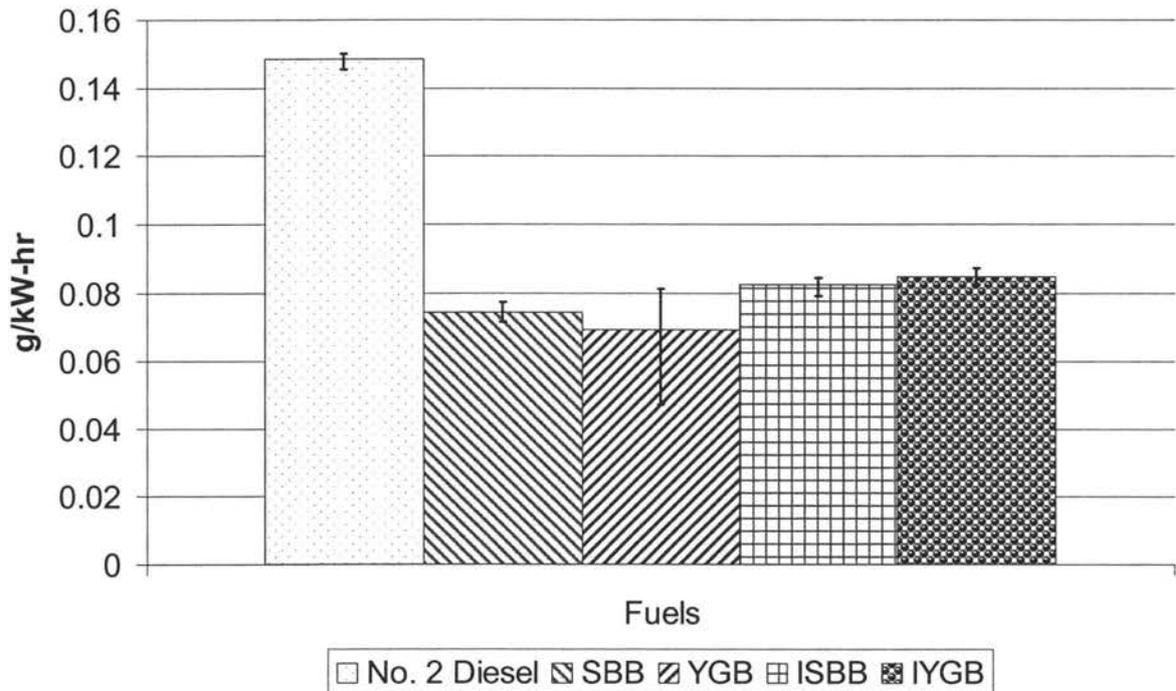


Figure 5.8: Brake specific HC emissions at 352.5 N-m and 1400 rpm

From Figure 5.8, No. 2 diesel fuel had the highest HC emission and the yellow grease methyl esters had the lowest HC emissions. While the yellow grease methyl esters had a 53.3% drop in HC emissions and yellow grease isopropyl esters only experienced a 42.9% drop, the means for all four biodiesels are not significantly different from each other. Canakci [7] reported a 46.3% and 42.5% drop for yellow grease methyl esters and soy methyl esters respectively when compared to No. 2 diesel fuel. Monyem [6] also found a significant drop of 53.2% when neat esters were used in a diesel engine.

5.2.5 Oxides of Nitrogen (NO_x) Emissions

While the other emissions for the various biodiesel fuels have been consistent, the NO_x emissions results are more variable. Figure 5.9 shows the means for the NO_x emissions at 352.5 N-m and 1400 rpm.

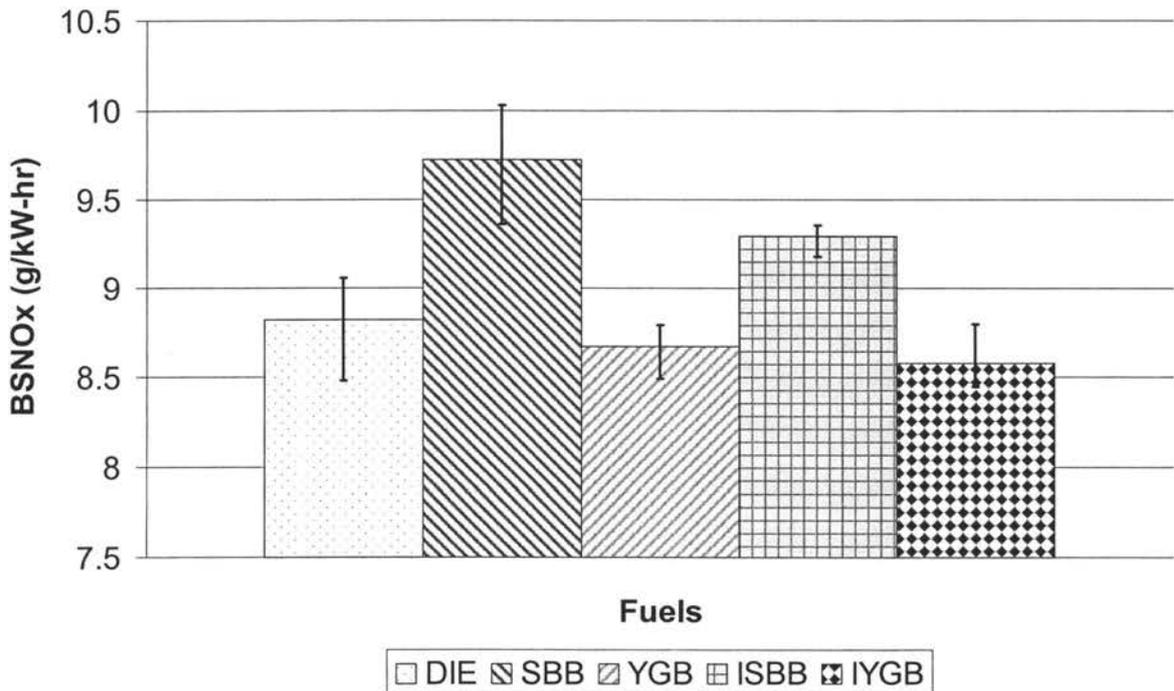


Figure 5.9: Brake Specific NO_x Emissions at 352.5 N-m and 1400 rpm

Observing Figure 5.9, the oxides of nitrogen emissions are lower for both yellow grease-based biodiesel fuels and higher for the soy oil-based biodiesel fuels. When comparing the means using the Tukey test, the 10.25% rise in NO_x emissions for soy oil methyl esters is statistically significant when compared to the base No. 2 diesel fuel.

Although there is a 5.37 % rise in NO_x emissions when comparing soy oil isopropyl esters to No. 2 diesel fuel, it is not statistically significant. Likewise, the NO_x emission of both the yellow grease-based biodiesel is not significantly different from that of No. 2 diesel fuel. When comparing the means of the NO_x emissions between methyl and isopropyl esters

originating from the same source material, whether it is yellow grease or soy oil, the means are not statistically different. These results suggest that the source material and not the type of ester affect the NO_x emissions. The results of the Tukey tests are presented in Table 5.10 below.

Table 5.10: Tukey Grouping for BSNO_x

Level		Mean (g/kW-h)
SBB	A	9.723
ISBB	A B	9.292
DIE	B C	8.819
YGB	B C	8.668
IYGB	C	8.578

While not statistically significant, the isopropyl esters had lower NO_x emissions compared to their methyl ester counterparts. It is also worthwhile to note that both soybean-based esters had an increase in NO_x emissions compared to No. 2 diesel fuel. When a Student t-test had been used to compare the means of ISBB and DIE, the p value was reported as 0.0608. This represents a 90% confidence level that the rise in NO_x emissions for ISBB is statistically significant when compared to No. 2 diesel fuel. It has been suggested that soy-based biodiesel can cause a rise in NO_x emissions [8]. The rise in NO_x emissions can also be attributed to the fact that biodiesel is an oxygenated fuel. The presence of additional oxygen in the fuel, about 10-11% by weight, may cause nitrogen to oxidize in lean combustion areas in the cylinder. Since isopropyl esters are heavier molecules, but still have the same number of oxygen atoms, the slight reduction in oxygen can lessen the NO_x emissions. Both the isopropyl esters are about 10% oxygen, by weight, while the methyl

esters are about 11% oxygen, by weight. However, this reduction in oxygen is only 1% and so the means in NO_x emissions are not significantly different, either.

McCormick et al. [8] also suggested that the increased NO_x emissions can be attributed to increasing fuel density or decreasing cetane number. Upon observing the trends in Figure 5.9 and their individual cetane numbers in Table 5.2, this trend is confirmed. IYGB had a cetane number of 65.6, the highest cetane number of all the fuels, yet its NO_x emissions were not significantly different from No. 2 diesel fuel. SBB had the lowest cetane number for all four fuels and had the highest NO_x emissions. Once again, this leads to the conclusion that the source material has the most to do with the changes in NO_x emissions.

5.2.6 Bosch Smoke Numbers

The smoke numbers for all fuels is graphically represented in Figure 5.10. All four biodiesels displayed significant reductions. The smoke numbers were lower by 43.57%, 39.42%, 37.76%, and 36.93% for SBB, YGB, ISBB, and IYGB respectively. The Tukey tests for comparison of the means show that the change is statistically significant. The difference in the means for both the isopropyl esters was not statistically significant. This was true for the methyl esters as well. For comparison, Monyem [6] reported a 56.9% drop in smoke number when using soybean methyl ester.

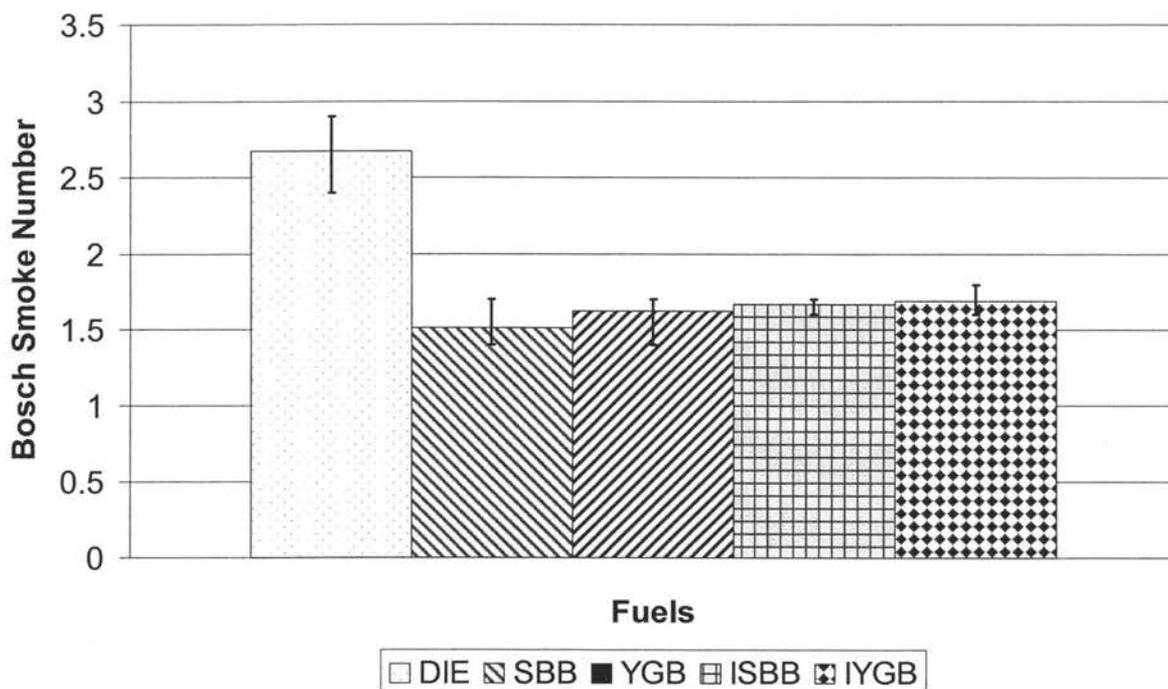


Figure 5.10: Bosch Smoke Numbers at 352.5 N-m and 1400 rpm.

The Tukey grouping for the means is presented in Table 5.11 below.

Table 5.11: Tukey Grouping for Smoke Number

<i>Level</i>		Mean (g/kW-h)
DIE	A	2.678
IYGB	B	1.689
ISBB	B	1.667
YGB	B C	1.622
SBB	C	1.511

5.2.7 Summary of Emissions Results

Overall, the emission results for isopropyl esters did not differ significantly when compared to methyl esters. There is some evidence that the lower oxygen content of the isopropyl esters lowers the NO_x emissions. There is stronger evidence, however, that the source material is more likely to affect emission characteristics.

6. CONCLUSIONS AND RECOMMENDATIONS

This chapter will summarize the conclusions from this study and provide some recommendations for future work.

6.1 Conclusions

The production of isopropyl ester was optimized to save on processing costs. By using less alcohol, savings can be made in terms of energy and equipment costs. Three different alcohol ratios were studied and it was found that a 20:1 isopropyl alcohol ratio works best for producing biodiesel within the standard specification for biodiesel fuel. One percent sodium metal based on the weight of the triglyceride was a suitable catalyst amount. Materials with high free fatty acid content were pretreated following the previous work done by Canakci [17] and finished up using the recipe above.

The fuels that were produced at BECON followed the same recipe except for the type of catalyst and the amount used. Potassium isopropoxide in isopropyl alcohol was purchased from Callery Chemical in Evans City, Pennsylvania. The amount was added such that 1.34% of potassium metal based on the weight of the triglyceride would be in the isopropyl alcohol. Both the fuels made in the lab and in BECON had trouble separating from the glycerol phase.

The effects of the isopropyl esters in engine testing are not significantly different from that of methyl esters. The exhaust emissions from the combustion of isopropyl esters in a diesel engine were lower in carbon monoxide, unburned hydrocarbons and smoke number when compared to No. 2 diesel fuel. The oxides of nitrogen were slightly higher for soy isopropyl esters and slightly lower for yellow grease isopropyl esters when compared to No. 2 diesel fuel. Statistically, the differences in NO_x emissions of No.2 diesel fuel and isopropyl

esters are not significant. We conclude that the lower oxygen content in isopropyl esters may have influenced the reduction in NO_x emissions.

6.2 Recommendations for Future Work

The following is a list of recommendations for future work with isopropyl esters.

1. Investigate the cold flow properties of isopropyl-methyl ester blends. If the cold flow properties of this blend are acceptable, neat isopropyl esters need not be used solely and this will minimize the cost of improving the cold flow properties of neat biodiesel.
2. Pure isopropyl esters from individual fatty acids should be produced and tested for cold flow properties such as pour point, cloud point, cold filter plugging point, as well as emission characteristics from combustion in a diesel engine.
3. A lot of water was used to aid the separation process of the glycerol, biodiesel and isopropyl alcohol. To further save on costs, work needs to be done to extract and recover the glycerol and the isopropyl alcohol from the mixture with the least amount of cost after transesterification.

APPENDIX A:**GAS CALIBRATION CURVES FOR THE EMISSION ANALYZERS**

The following graphs in this appendix section were produced by running span gases with known concentrations through the analyzers. The readings from the front panels of the analyzers or from the data acquisition system are represented on the x-axes and the actual concentration of the gas is represented in the y-axes. Appendix C presents the raw data that was read from the front panels or from the data acquisition system. The data was processed using the fits obtained from the following curves.

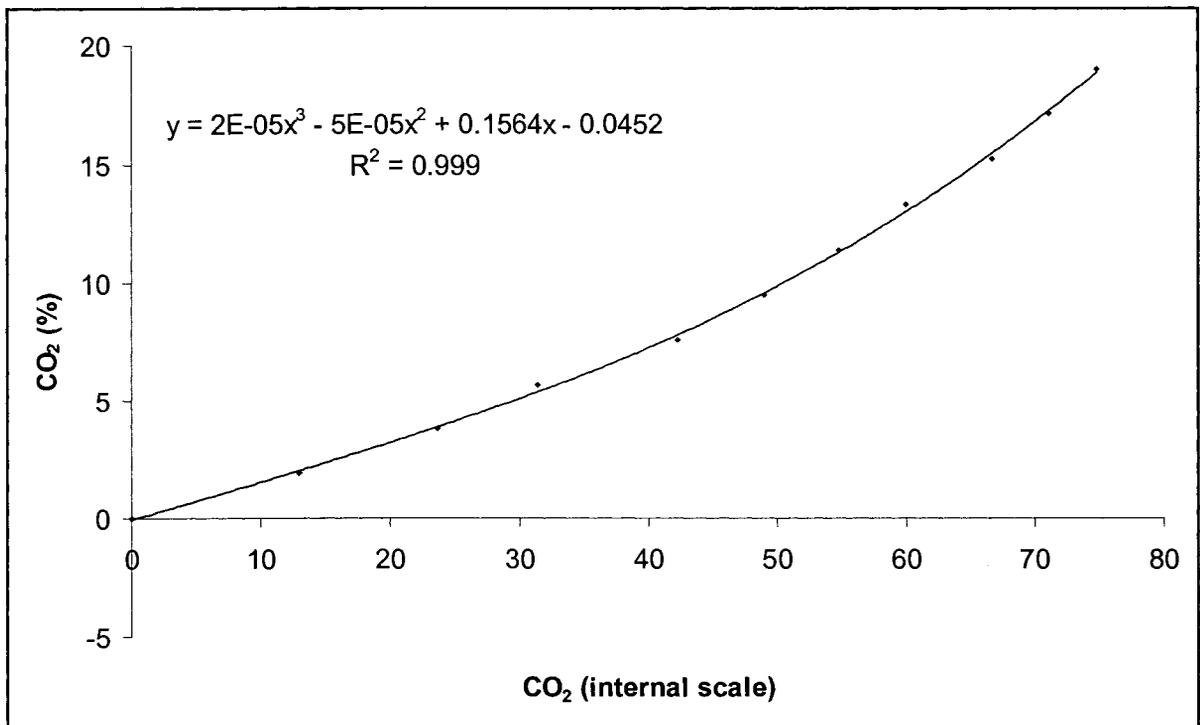


Figure A.1: Calibration Curve of CO₂ analyzer

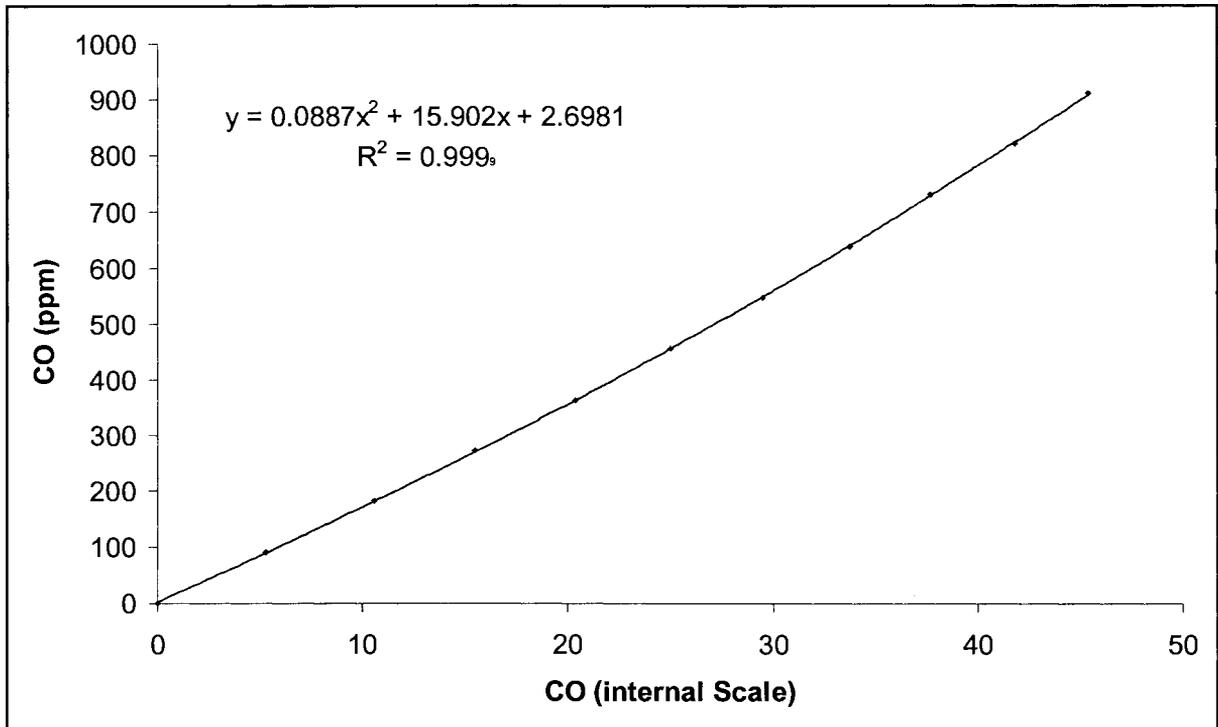


Figure A.2: Calibration curve of CO analyzer

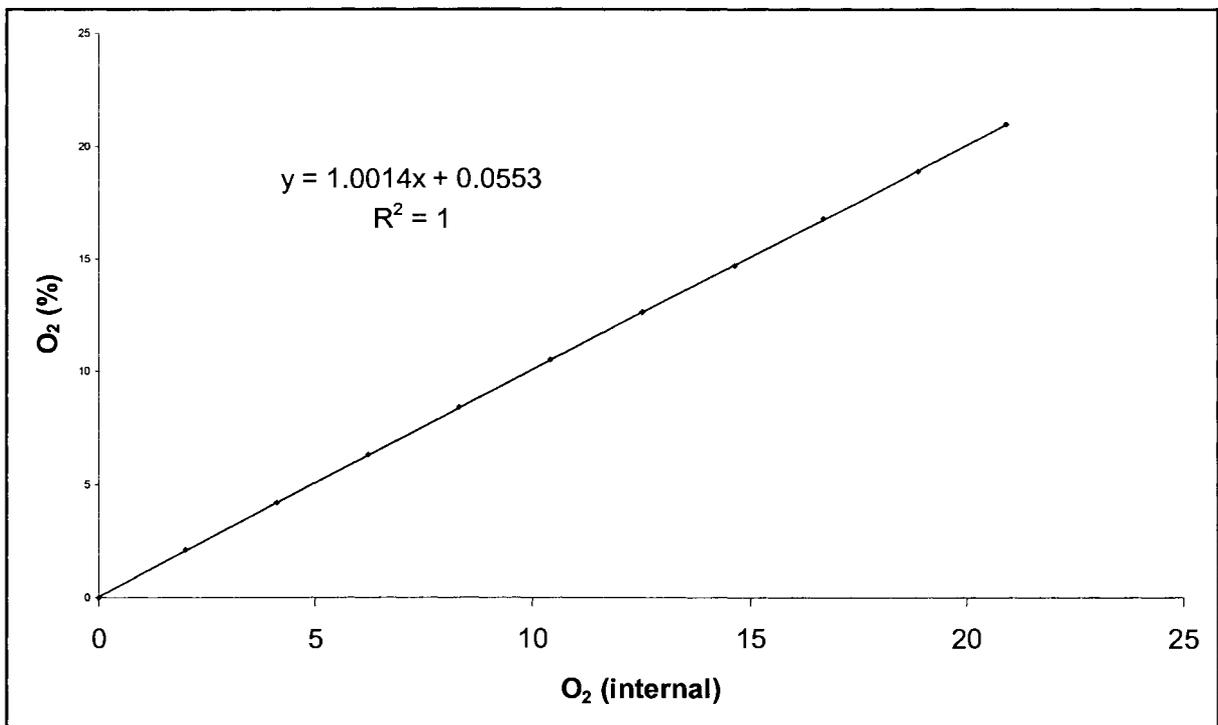


Figure A.3: Calibration curve of O₂ analyzer

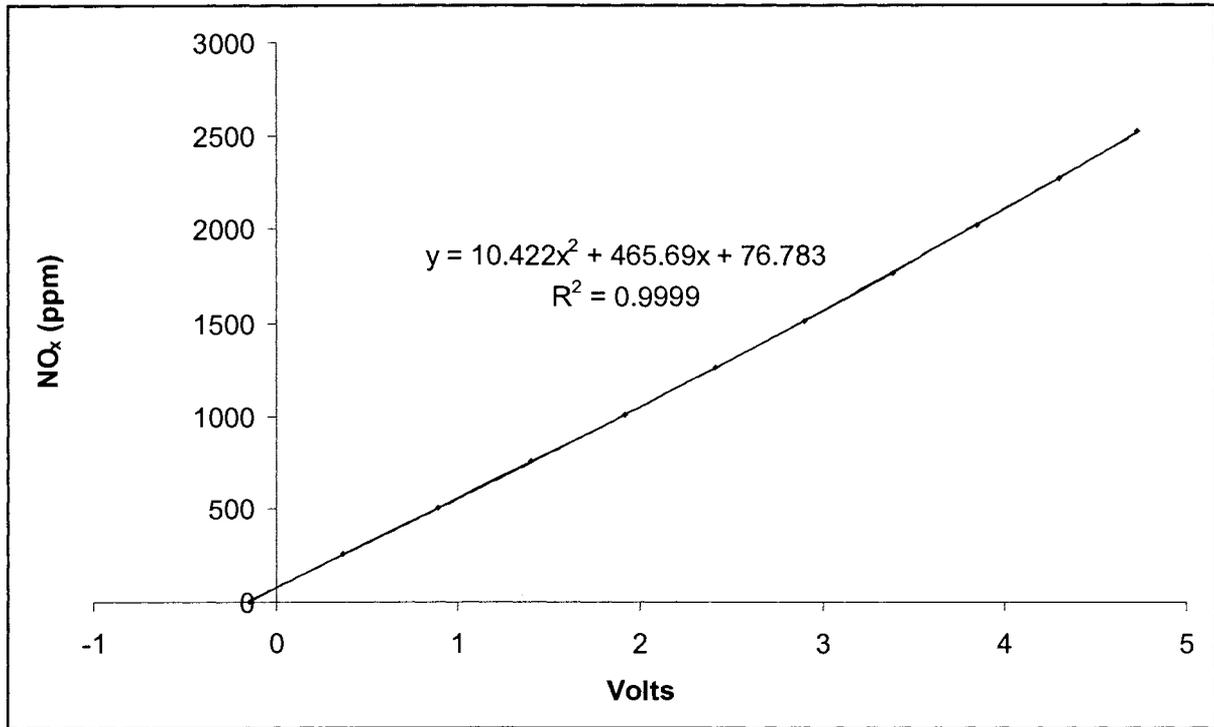


Figure A.4: Calibration Curve for NO_x Analyzer

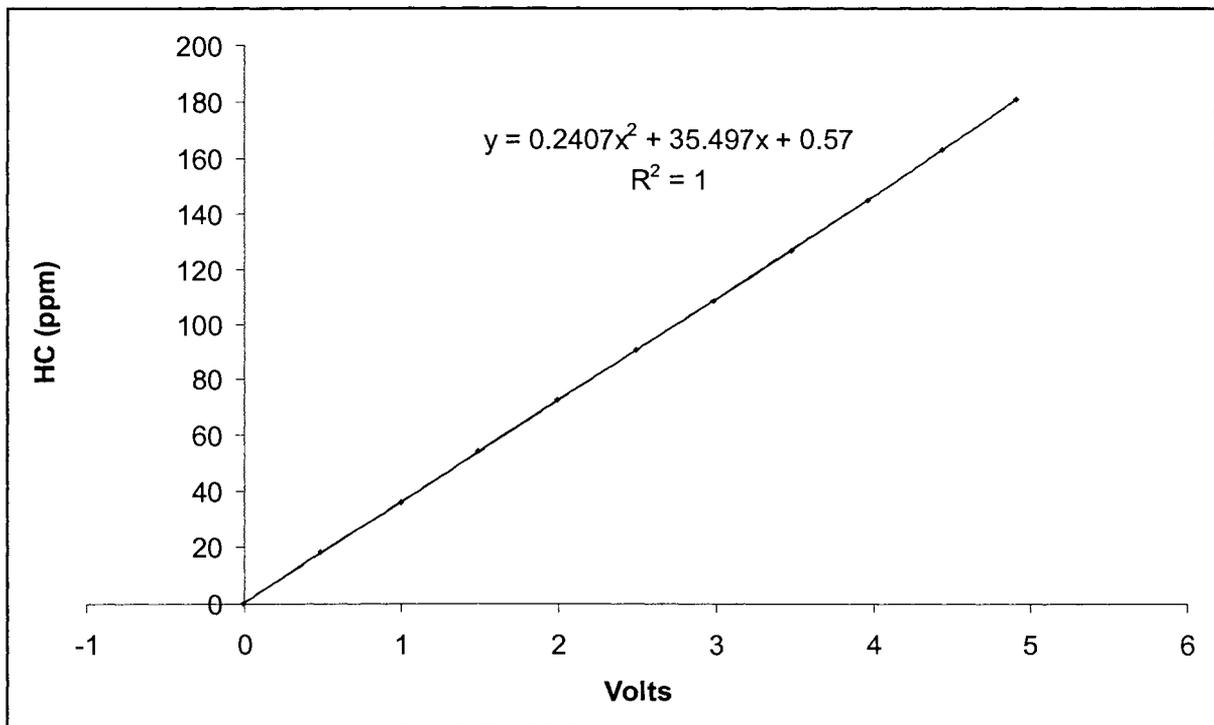


Figure A.5: Calibration Curve for HC Analyzer

APPENDIX B:
ANOVA TABLES

An analysis of variance was done for the data on each of the individual pollutants. The outputs presented here are from JMP, a statistical software package. In the following tables, DF represents the degrees of freedom, LSD represents the Least Significant Difference, and HSD represents Honestly Significant Difference. As is stated below, $\alpha = 0.05$, which represents a 95% confidence interval. The quantile that is used to scale the LSD is represented by q^* . The report presented also includes the comparison for all pairs of means using the Tukey HSD Method.

REPORT B.1: Statistical Analysis for BSCO₂

Oneway ANOVA

Summary of Fit

Rsquare	0.323603
Adj Rsquare	0.053044
Root Mean Square Error	5.601317
Mean of Response	721.6797
Observations (or Sum Wgts)	15

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Fuel	4	150.10341	37.5259	1.1961	0.3707
Error	10	313.74750	31.3748		
C. Total	14	463.85091			

Means for Oneway ANOVA

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
DIE	3	724.418	3.2339	717.21	731.62
ISBB	3	724.686	3.2339	717.48	731.89
IYGB	3	718.807	3.2339	711.60	726.01
SBB	3	723.493	3.2339	716.29	730.70
YGB	3	716.994	3.2339	709.79	724.20

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	ISBB	DIE	SBB	IYGB	YGB
ISBB	0.0000	0.2678	1.1928	5.8787	7.6922
DIE	-0.2678	0.0000	0.9251	5.6109	7.4244
SBB	-1.1928	-0.9251	0.0000	4.6859	6.4994
IYGB	-5.8787	-5.6109	-4.6859	0.0000	1.8135
YGB	-7.6922	-7.4244	-6.4994	-1.8135	0.0000

Alpha=
0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
3.29108	0.05

Abs(Dif)-LSD	ISBB	DIE	SBB	IYGB	YGB
ISBB	-15.052	-14.784	-13.859	-9.173	-7.359
DIE	-14.784	-15.052	-14.127	-9.441	-7.627
SBB	-13.859	-14.127	-15.052	-10.366	-8.552
IYGB	-9.173	-9.441	-10.366	-15.052	-13.238
YGB	-7.359	-7.627	-8.552	-13.238	-15.052

Positive values show pairs of means that are significantly different.

Level		Mean
ISBB	A	724.68597
DIE	A	724.41818
SBB	A	723.49313
IYGB	A	718.80725
YGB	A	716.99376

Levels not connected by same letter are significantly different

REPORT B.2: Statistical Analysis for BSCO

Oneway Analysis of BSCO

Summary of Fit

Rsquare	0.960134
Adj Rsquare	0.942416
Root Mean Square Error	0.038255
Mean of Response	1.073276
Observations (or Sum Wgts)	14

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Fuel	4	0.31721923	0.079305	54.1898	<.0001
Error	9	0.01317118	0.001463		
C. Total	13	0.33039041			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
DIE	2	1.32842	0.02705	1.2672	1.3896
ISBB	3	1.19190	0.02209	1.1419	1.2419
IYGB	3	1.08279	0.02209	1.0328	1.1328
SBB	3	0.88113	0.02209	0.8312	0.9311
YGB	3	0.96717	0.02209	0.9172	1.0171

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	DIE	ISBB	IYGB	YGB	SBB
DIE	0.00000	0.13652	0.24563	0.36125	0.44729
ISBB	-0.13652	0.00000	0.10911	0.22473	0.31077
IYGB	-0.24563	-0.10911	0.00000	0.11562	0.20166
YGB	-0.36125	-0.22473	-0.11562	0.00000	0.08604
SBB	-0.44729	-0.31077	-0.20166	-0.08604	0.00000

Alpha=
0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
3.36259	0.05

Abs(Dif)-LSD	DIE	ISBB	IYGB	YGB	SBB
DIE	-0.12864	0.01909	0.12820	0.24382	0.32986
ISBB	0.01909	-0.10503	0.00408	0.11970	0.20574
IYGB	0.12820	0.00408	-0.10503	0.01059	0.09663
YGB	0.24382	0.11970	0.01059	-0.10503	-0.01899
SBB	0.32986	0.20574	0.09663	-0.01899	-0.10503

Positive values show pairs of means that are significantly different.

Level				Mean
DIE	A			1.3284243
ISBB		B		1.1919038
IYGB			C	1.0827922
YGB			D	0.9671722
SBB			D	0.8811350

Levels not connected by same letter are significantly different

REPORT B.3: Statistical Analysis for BSNO_x

Oneway Analysis of BSNO_x By Fuel Summary of Fit

Rsquare	0.83543
Adj Rsquare	0.769601
Root Mean Square Error	0.234177
Mean of Response	9.015917
Observations (or Sum Wgts)	15

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Fuel	4	2.7838640	0.695966	12.6911	0.0006
Error	10	0.5483903	0.054839		
C. Total	14	3.3322543			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
DIE	3	8.81876	0.13520	8.5175	9.120
ISBB	3	9.29245	0.13520	8.9912	9.594
IYGB	3	8.57766	0.13520	8.2764	8.879
SBB	3	9.72269	0.13520	9.4214	10.024
YGB	3	8.66802	0.13520	8.3668	8.969

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	SBB	ISBB	DIE	YGB	IYGB
SBB	0.0000	0.4302	0.9039	1.0547	1.1450
ISBB	-0.4302	0.0000	0.4737	0.6244	0.7148
DIE	-0.9039	-0.4737	0.0000	0.1507	0.2411
YGB	-1.0547	-0.6244	-0.1507	0.0000	0.0904
IYGB	-1.1450	-0.7148	-0.2411	-0.0904	0.0000

Alpha=
0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
3.29108	0.05

Abs(Dif)-LSD	SBB	ISBB	DIE	YGB	IYGB
SBB	-0.62927	-0.19903	0.27465	0.42539	0.51575
ISBB	-0.19903	-0.62927	-0.15559	-0.00485	0.08551
DIE	0.27465	-0.15559	-0.62927	-0.47853	-0.38817
YGB	0.42539	-0.00485	-0.47853	-0.62927	-0.53891
IYGB	0.51575	0.08551	-0.38817	-0.53891	-0.62927

Positive values show pairs of means that are significantly different.

Level				Mean
SBB	A			9.7226860
ISBB	A	B		9.2924471
DIE		B	C	8.8187641
YGB		B	C	8.6680244
IYGB			C	8.5776649

Levels not connected by same letter are significantly different

REPORT B.4: Statistical Analysis for BSHC

Oneway Analysis of BSHC By Fuel

Summary of Fit

Rsquare	0.940217
Adj Rsquare	0.916303
Root Mean Square Error	0.008912
Mean of Response	0.091945
Observations (or Sum Wgts)	15

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Fuel	4	0.01249006	0.003123	39.3177	<.0001
Error	10	0.00079417	0.000079		
C. Total	14	0.01328423			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
DIE	3	0.148572	0.00515	0.13711	0.16004
ISBB	3	0.082589	0.00515	0.07112	0.09405
IYGB	3	0.084826	0.00515	0.07336	0.09629
SBB	3	0.074369	0.00515	0.06290	0.08583
YGB	3	0.069371	0.00515	0.05791	0.08084

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	DIE	IYGB	ISBB	SBB	YGB
DIE	0.00000	0.06375	0.06598	0.07420	0.07920
IYGB	-0.06375	0.00000	0.00224	0.01046	0.01545
ISBB	-0.06598	-0.00224	0.00000	0.00822	0.01322
SBB	-0.07420	-0.01046	-0.00822	0.00000	0.00500
YGB	-0.07920	-0.01545	-0.01322	-0.00500	0.00000

Alpha=
0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
3.29108	0.05

Abs(Dif)-LSD	DIE	IYGB	ISBB	SBB	YGB
DIE	-0.02395	0.03980	0.04204	0.05026	0.05525
IYGB	0.03980	-0.02395	-0.02171	-0.01349	-0.00849
ISBB	0.04204	-0.02171	-0.02395	-0.01573	-0.01073
SBB	0.05026	-0.01349	-0.01573	-0.02395	-0.01895
YGB	0.05525	-0.00849	-0.01073	-0.01895	-0.02395

Positive values show pairs of means that are significantly different.

Level		Mean
DIE	A	0.14857219
IYGB	B	0.08482610
ISBB	B	0.08258889
SBB	B	0.07436887
YGB	B	0.06937118

Levels not connected by same letter are significantly different

REPORT B.5: Statistical Analysis for Smoke Numbers

**Oneway Analysis of Smoke
Summary of Fit**

Rsquare	0.948045
Adj Rsquare	0.94285
Root Mean Square Error	0.105935
Mean of Response	1.833333
Observations (or Sum Wgts)	45

Analysis of Variance

Source	DF	Sum of Squares	Mean Square	F Ratio	Prob > F
Fuel	4	8.1911111	2.04778	182.4752	<.0001
Error	40	0.4488889	0.01122		
C. Total	44	8.6400000			

Means for Oneway Anova

Level	Number	Mean	Std Error	Lower 95%	Upper 95%
DIE	9	2.67778	0.03531	2.6064	2.7491
ISBB	9	1.66667	0.03531	1.5953	1.7380
IYGB	9	1.68889	0.03531	1.6175	1.7603
SBB	9	1.51111	0.03531	1.4397	1.5825
YGB	9	1.62222	0.03531	1.5509	1.6936

Std Error uses a pooled estimate of error variance

Means Comparisons

Dif=Mean[i]-Mean[j]	DIE	IYGB	ISBB	YGB	SBB
DIE	0.0000	0.9889	1.0111	1.0556	1.1667
IYGB	-0.9889	0.0000	0.0222	0.0667	0.1778
ISBB	-1.0111	-0.0222	0.0000	0.0444	0.1556
YGB	-1.0556	-0.0667	-0.0444	0.0000	0.1111
SBB	-1.1667	-0.1778	-0.1556	-0.1111	0.0000

Alpha=
0.05

Comparisons for all pairs using Tukey-Kramer HSD

q*	Alpha
2.85609	0.05

Abs(Dif)-LSD	DIE	IYGB	ISBB	YGB	SBB
DIE	-0.1426	0.8463	0.8685	0.9129	1.0240
IYGB	0.8463	-0.1426	-0.1204	-0.0760	0.0351
ISBB	0.8685	-0.1204	-0.1426	-0.0982	0.0129
YGB	0.9129	-0.0760	-0.0982	-0.1426	-0.0315
SBB	1.0240	0.0351	0.0129	-0.0315	-0.1426

Positive values show pairs of means that are significantly different.

Level				Mean
DIE	A			2.677778
IYGB		B		1.688889
ISBB		B		1.666667
YGB		B	C	1.622222
SBB			C	1.511111

Levels not connected by same letter are significantly different

APPENDIX C:

Raw Data Collected from Engine Tests

Table C.1: Raw Data from First Run

Fuel	DIE 1	YGB 1	ISBB1	SBB1	IYGB1
Patm (mm Hg)	738	738	738	738	738
Engine Speed	1400	1400	1400	1400	1400
Load (%)	95%	95%	95%	95%	95%
Brake Torque (lb-ft)	260.0	260.5	259.5	260.0	260.0
ΔP of LFE (" H ₂ O)	2.475	2.48	248	2.48	2.5
Coolant Count (10 cps)	141.7	135	145.9	140.2	135.8
Temperatures (°F)					
1. Engine Oil	210	210	211	210	209
2. Eng. CW Out Temp	176	177	178	177	177
3. Eng. CW Inlet Temp	158	157	158	157	157
4. Bldg. CW Inlet Temp	51	52	52	52	52
5. Bldg. CW Outlet Temp	77	76	79	77	76
6. Intake Air Temp	75	75	76	77	77
7. Intake Manifold Temp	138	138	139	139	139
8. Exhaust Temp.	1004	985	994	982	986
oil presure (psi)	48	48	48	48	48
Boost pressure (psi)	4.0	4.0	4.0	3.8	3.7
Emissions					
wet bulb temp (°F)	61	61	61	61	61
dry bulb temp (°F)	72	72	72	72	72
O ₂ (%)	6.35	6.405	6.32	6.445	6.365
CO (%)	14.8	14.8	17.25	13	15.6
CO ₂ (%)	56.5	56.4	56.7	56.4	56.3
HC (Volts) ^a	0.71	0.22	0.42	0.38	0.41
NO _x (Volts) ^b	2.29	2.28	2.55	2.565	2.29
Fuel Cons. (g/min)	180.3916	204.8235	204.6766	203.6683	201.1727
ΔW (g)	2188	1281	1437	1351	1298
time (min)	12	6	7	6	6
time (s)	7.75	15.25	1.25	38	27.13
total time (s)	727.75	375.25	421.25	398	387.13

^aTo convert from volts to ppm, refer to Figure A.5 in Appendix A.

^bTo convert from volts to ppm, refer to Figure A.4 in Appendix A.

Table C.2: Raw Data from Second Run

Fuel	YGB2	SBB2	ISBB2	IYGB2	DIE 2
Patm (mm Hg)	738	738	738	738	738
Engine Speed	1400	1400	1400	1400	1400
Load (%)	95%	95%	95%	95%	95%
Brake Torque (lb-ft)	260.0	261.0	260.0	260.5	259.5
ΔP of LFE (" H ₂ O)	2.48	2.5	2.48	2.45	2.48
Coolant Count (10 cps)	135.9	135.9	140	139.8	151.5
Temperatures (F)					
1. Engine Oil	210	209	211	210	209
2. Eng. CW Out Temp	177	177	178	177	177
3. Eng. CW Inlet Temp	157	157	158	158	159
4. Bldg. CW Inlet Temp	52	52	52	52	52
5. Bldg. CW Outlet Temp	77	76	76	77	77
6. Intake Air Temp	77	76	76	76	76
7. Intake Manifold Temp	139	138	139	139	140
8. Exhaust Temp.	980	981	987	988	1003
oil pressure (psi)	48	48	48	48	48
Boost pressure (psi)	3.8	3.8	3.8	3.8	4.0
Emissions					
wet bulb temp (°F)	62	62	62	62	62
dry bulb temp (°F)	71	71	71	71	71
O ₂ (%)	6.435	6.48	6.305	6.32	6.26
CO (%)	13.75	12.45	17	15.85	19.05
CO ₂ (%)	56.2	56.5	56.6	56.5	56.55
HC (Volts) ^a	0.38	0.36	0.42	0.4	0.745
NO _x (Volts) ^b	2.34	2.605	2.465	2.355	2.4
Fuel Cons. (g/min)	204.7059	205.1201	201.9531	202.4626	182.9207
ΔW (g)	1218	1513	1165	940	1086
time (min)	5	7	5	4	5
time (s)	57	22.57	46.12	38.57	56.22
total time (s)	357	442.57	346.12	278.57	356.22

^aTo convert from volts to ppm, refer to Figure A.5 in Appendix A.

^bTo convert from volts to ppm, refer to Figure A.4 in Appendix A.

Table C.3: Raw Data from Third Run

Fuel	ISBB3	DIE 3	SBB 3	IYGB3	YGB3
Patm (mm Hg)	738	738	738	738	738
Engine Speed	1400	1400	1400	1400	1400
Load (%)	95%	95%	95%	95%	95%
Brake Torque (lb-ft)	260.5	260.0	260.5	260.0	260.0
ΔP of LFE (" H ₂ O)	2.45	2.48	2.48	2.48	2.45
Coolant Count (10 cps)	142	153.4	138.8	137.5	139.1
Temperatures (F)					
1. Engine Oil	210	210	211	211	210
2. Eng. CW Out Temp	178	177	177	177	177
3. Eng. CW Inlet Temp	158	159	157	157	158
4. Bldg. CW Inlet Temp	51	52	51	52	52
5. Bldg. CW Outlet Temp	77	77	76	76	76
6. Intake Air Temp	76	76	76	78	76
7. Intake Manifold Temp	139	140	138	139	139
8. Exhaust Temp.	987	1006	982	988	979
oil pressure (psi)	48	48	48	48	48
Boost pressure (psi)	3.8	4.0	3.7	3.6	3.6
Emissions					
wet bulb temp (°F)	62.5	62.5	62.5	62.5	62.5
dry bulb temp (°F)	71	71	71	71	71
O ₂ (%)	6.38	6.18	6.48	6.325	6.455
CO (%)	18.15	19.5	13.9	16.55	14.6
CO ₂ (%)	56.65	56.6	56.5	56.45	56.3
HC (Volts) ^a	0.385	0.74	0.345	0.44	0.395
NO _x (Volts) ^b	2.46	2.365	2.585	2.24	2.32
Fuel Cons. (g/min)	203.2633	182.069	204.4045	205.1813	204.0601
ΔW (g)	980	990	1137	1155	1032
time (min)	4	5	5	5	5
time (s)	49.28	26.25	33.75	37.75	3.44
total time (s)	289.28	326.25	333.75	337.75	303.44

^aTo convert from volts to ppm, refer to Figure A.5 in Appendix A.

^bTo convert from volts to ppm, refer to Figure A.4 in Appendix A.

Table C.4: Smoke Number Data

smoke	1	2	3
<i>DIE 1</i>	2.6	2.6	2.4
<i>YGB 1</i>	1.6	1.4	1.7
<i>ISBB1</i>	1.7	1.6	1.7
<i>SBB1</i>	1.7	1.6	1.5
<i>IYGB1</i>	1.7	1.7	1.7
<i>YGB2</i>	1.6	1.6	1.7
<i>SBB2</i>	1.5	1.5	1.4
<i>ISBB2</i>	1.6	1.7	1.6
<i>IYGB2</i>	1.7	1.7	1.6
<i>DIE 2</i>	2.8	2.6	2.5
<i>ISBB3</i>	1.7	1.7	1.7
<i>DIE 3</i>	2.8	2.9	2.9
<i>SBB 3</i>	1.5	1.5	1.4
<i>IYGB3</i>	1.8	1.7	1.6
<i>YGB3</i>	1.6	1.7	1.7

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