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Analysis of the Performance of Peanut Fame in a Single Cylinder Idi Engine and Investigations of Neat Methyl Ester Influence on Fuel Quality

Jeffery Lewis

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ANALYSIS OF THE PERFORMANCE OF PEANUT FAME IN A SINGLE CYLINDER IDI ENGINE AND INVESTIGATIONS OF NEAT METHYL ESTER INFLUENCE ON FUEL QUALITY

by

JEFFERY LEWIS

(Under the Direction of Valentin Soloiu)

ABSTRACT

To meet evolving standards set forth by the U.S. EPA and U.S. Energy Policy it is necessary to consider a variety of feedstock for biofuels synthesis and to understand the role individual fatty acids contribute to the overall performance. It is the belief of the authors that excess peanut production would provide an excellent source for high quality biodiesel feedstock, and the complete property and combustion analysis of the fatty acid components will provide insight for future biofuel developments. The preliminary investigations of the project focused on the combustion performance and thermal efficiency of peanut FAME and its main FAME component the methyl oleate using a single cylinder naturally aspirated compression ignition engine. The ignition delay at 2200 rpm, 4.78 bmep (100% load) remained constant for all biodiesel-diesel blends tested. The rate of heat release for 50 % peanut FAME diesel blend (P50) reached a slightly higher maximum of $20.0 \text{ J/Crank Angle Degrees (CAD)}$ $D_{100}$ at $17.5 \text{ J/CAD}$. The heat release rate for O50 attained a slightly lower maximum at $15.5 \text{ J/CAD}$ versus $17.5 \text{ J/CAD}$ for $D_{100}$. The combustion duration decreased by approximately 5 CAD from $D_{100}$ to P50 and O50. The analysis of mechanical efficiency while operating with peanut FAME diesel blends indicated a 4 % loss over the transition from $D_{100}$ to P50. The engine’s mechanical efficiency using O50 decreased by 8 % compared to $D_{100}$ and the overall efficiency of the engine remained constant for all tested fuels at the same speed and bmep. Preliminary findings support peanut FAME as a viable option when blended and used with diesel engines and begins to account the effect methyl oleate has on the performance of the full bodied peanut FAME.

INDEX WORDS: Biodiesel, Peanuts, Combustion, Emissions, Transesterification, Compression ignition engines
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by

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2011
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DEDICATION

My Family
ACKNOWLEDGMENTS

Georgia Southern University
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NOMENCLATURES

A constant in Annand model

C_m piston average speed (m/s)

CAD crank angle degree (deg.)

D engine bore (m)

N engine speed (rpm)

P pressure (Pa)

Re in-cylinder Reynolds number (-)

S engine stroke (m)

T_A cylinder volume-averaged instantaneous gas temperature (K)

T_W cylinder wall average temperature (K)

V instantaneous volume (L)

α crank angle (deg.)

ε emissivity (-)

λ_A convection heat transfer coefficient (W/m^2K)

μ air dynamic viscosity (kg/s/m)

ρ air density (kg/m^3)

σ constant of proportionality (J/sm^3K^4)

γ ratio of specific heats

q heat flux (MW/m^2)

BTDC before top dead center

U.S. DOT United States Department of Transportation

cP centi Poise
bmep brake mean effective pressure

EEC

J/CAD Joules per crank angle degree

μV micro Volt relative energy required to maintain temperature gradient

K Kelvin

EGR exhaust gas recirculation

cSt centi Stokes

cP centi Poise

LPG liquefied petroleum gas

TGA thermo gravimetric analysis

DTA differential thermal analysis

SEM scanning electron microscope

Rpm rotations per minute

MPa mega Pascals

SMD Sauter mean diameter

pC/bar pico Coulomb per bar

FSO full scale output

FS full scale

bioCOM charcoal oil mixture

TDC top dead center

ppm parts per million

FSN filter smoke number
Chapter 1

Overview of the Study

Introduction

Over the next chapter an explanation of the addressed problem and the need for this problem to be studied will be presented. Together with these topics, the proposed goals and predicted outcomes will be discussed along with some initial issues faced during the first stages of the research. To help in providing a more complete understanding to the reader, the research limitations and a list of common terms and abbreviations will be defined.

Statement of the Problem

As the global energy demand increases it will become necessary to utilize renewable fuel sources to lessen the growing environmental impact and to realize national energy security. To contribute to the alleviation of this problem, the aim of this study was to investigate peanut fatty acid methyl esters from excess production in an indirect injection compression ignition engine and to determine the role neat fatty acid methyl esters play in the overall performance of the full bodied fuel, for petroleum diesel displacement and future biodiesel reformulation.

Statement of Need

In recent years a significant increase interest in renewable energy and its applications has been seen. A major contributing factor to this is the prediction of an upcoming peak oil production and ever rising prices of gasoline and diesel fuel. Current best estimations propose a peak that will happen between now and 2040 (GAO 2007).
The large timeline is due to the multiple and variable factors that contribute to such a calculation. In opposition the global demand for energy will steadily increasing due to the rising standards of living of large population centers such as India and China. These circumstances depict the need for a substantial investment in an alternative to fossil fuel energy infrastructure in order to meet this demand. As a part of this transition biodiesel, from vegetable and animal fats, is in a position to become a major contributor to the solution. Benefits of biodiesel include topics of recent increased importance such as energy security, renewability, sustainability, environmentally friendly, increased safety, enhanced lubrication effects, and a reduction of exhaust emissions in general, and miscibility with petroleum diesel for straightforward fossil fuel displacement.

Another need for such a study is growing concern over the climates changes caused by the excess emissions of greenhouse gases (GHG). Reports from the U.S. DOT, have cited that without additional climate polices the baseline human source GHG emissions could increase 25% to 90% from 2000 to 2030 (EIA, 2009). In particular, CO₂ from energy use could increase 40% to 110% over the same period. If such increases are experienced, the global temperature could rise between 1 °C to 6.5 °C by the end of the century. Increases in global temperature would lead to a sea level to raise anywhere from 0.2 m to 0.6 m, with recent estimates that include polar ice sheet melting to a possible 0.9 m to 1.2 m sea level rise. It has been proposed, in the U.S. DOT Synthesis Report, that a 50 % to 80 % GHG reduction by 2050 would help to limit global warming to 2-2.4 °C. A goal as demanding as this will require a multi-generational effort to reduce GHG emissions.
The need to reduce the dependence on fossil fuels has increased dramatically and while the necessary technologies and opportunities to significantly reduce the dependence on crude oil and other fossil fuels exist, they have not been implemented fully (Kammen D.M., Kapadia K., Fripp M. 2004). Given the myriad sources and opportunities afforded by alternate energy, bio-fuels lend themselves most readily to widespread adoption due to their adaptability to the current state of technology. Though the U.S. is still behind the European Union, which has been using 5% biodiesel mixed with regular diesel since the early 90’s, recent legislations help to ensure that the U.S. becomes a frontrunner in the alternative fuels industry.

**The Purpose of Study**

The dual purpose of this study was to determine the effect peanut fatty acid methyl esters, from excess peanut production, have on the combustion and emissions performance in an IDI CI engine with a separate combustion chamber and to investigate the effect neat methyl esters contribute to the fuel characteristics of full bodied biofuels.

**The Subproblems**

Before the objectives of this study could be completed, related issues needed to be resolved. The subproblems of this study were:

1. Determination of proper transesterification conditions for successful of peanut oil to peanut fatty acid methyl esters.
2. Development of a method for viscosity and shear stress testing of fuels over a temperature gradient.
3. Calculation of the Lower Heating Value (LHV) of the tested fuels for use in the thermodynamic calculations.

4. Determination of proper conditions for analysis of rate of mass loss, evaporation (endothermic reactions), and oxidation (exothermic reactions) for the tested fuels.

5. Determination of dynamometer, engine, and data acquisition operation conditions within acceptable ranges.

The Hypothesis

Excess peanut production is a viable feedstock for biodiesel synthesis and does not impose drastic performance issues in a single cylinder separate combustion chamber CI engine and the use of methyl oleate as a surrogate for biodiesel reformulation will enhance the performance in compression ignition engines.

Limitations

The limitations and controls used in fuel property and combustion investigations were as follows:

1. A 6:1 molar ratio of methanol to peanut oil, 1 wt.% of sodium hydroxide to peanut oil, reaction temperature of 65 °C, and reaction duration of 1 hour were needed to produce peanut fatty acid methyl esters.

2. The working fluid used for producing a temperature gradient during viscosity and shear stress testing could not go above 100 °C.

3. The sample size used for calorimeter tests must be between 0.5 to 0.8 grams.

4. The oxidation gas used for thermal analysis must be dry air.

5. The flow rate of oxidation gas used for thermal analysis must be # mL/min.
6. The temperature gradient used for thermal analysis must be \( \# \, ^{\circ}C/min \)

7. The sample size used for thermal analysis must be between 9 to 13 milligrams.

8. The smoke meter must be turned on, for warm-up, 30 minutes before engine data collection begins.

9. The charge amplifier for the pressure sensor must be turned on, for warm-up, 15 minutes before engine data collection begins.

10. The NOx sensor must be running whenever the engine is running to prevent O\(_2\) sensor fouling.

11. The ambient temperature must be maintained between 20 \( ^{\circ}C \) and 25 \( ^{\circ}C \).

12. The dynamometer oil temperature must be maintained between 38 \( ^{\circ}C \) and 42 \( ^{\circ}C \).

13. The engine oil temperature must be maintained between 80 \( ^{\circ}C \) and 100 \( ^{\circ}C \).

**Procedure**

The procedure followed for this study was as follows:

1. The topic of combustion of peanut fatty acid methyl esters in a CI engine was investigated.

2. The topic of the influence of chemical structure on fatty acid methyl ester properties and combustion characteristics was investigated.

3. Established peanut fatty acid methyl ester synthesis process at Georgia Southern University.

4. Established viscosity and shear stress testing procedures of fuels at Georgia Southern University.
5. Established calorimeter testing procedures of fuels at Georgia Southern University.

6. Established thermo gravimetric and differential thermal analysis procedures of fuels at Georgia Southern University.

7. A theoretical thermodynamic engine model was utilized for comparison to collected data.

8. Engine investigations were conducted and data was collected associated with combustion performance.

9. Collected data was used in determination of injection phenomenon, heat transfer, heat generation, lambda, ignition delay, power production, mechanical and overall efficiency, specific fuel consumption, NOx emissions, and particulate matter emissions.

10. Findings were analyzed based on topics studied and reviewed.

11. The findings of the investigations were compiled and accounted.

Definitions and Abbreviations

The definition of terms and their abbreviations used in this study were defined in alphabetical order as follows:

Air to Fuel Ratio (A/F) - the amount of air to fuel ratio, usually referred to by volume or by mass. In this study, this term is used for both volume and mass units.

Brake Specific Fuel Consumption (BSFC) - the amount of fuel necessary (mass) to produce one kW*hr of power. (g/kW*hr)
Before Top Dead Center (BTDC) - point of reference for the location of the piston in its stroke, usually has a numerical value referring to the crank angle degrees of rotation necessary for the piston to achieve its top most location.

Crank Angle Degrees (CAD) - a numerical value representing degrees of rotation of the engine crankshaft.

Compression Ignition (CI) - one of the two main types of internal combustion engines; ignition of fuel is caused due to high pressure, also referred to as a diesel engine.

Data Acquisition (DAQ) - the process of collecting electrical signals from sensors that measure physical conditions, represented in numerical values.

Direct Injection (DI) – a form of injection system in a diesel engine where fuel is injected directly into the main combustion chamber of an engine.

Dynamometer – a tool used to apply a resistive load to an engine and determine the amount of power and torque the engine is able to produce; also referred to in short as a dyno.

Encoder – a transducer that is used to measure crank angle rotation.

Fatty Acid Methyl Esters (FAME) – biodiesel made from animal fat that contains fatty acids attached to methyl esters.

Internal Combustion (IC) – an engine where combustion takes place inside of a chamber.

Indirect Injection (IDI) – a type of injection system used in some diesel engines; fuel is injected into a separate combustion chamber instead of directly into the main combustion chamber.
Lower Heating Value (LHV) – the amount of energy released during combustion of a given amount of fuel

Nitrogen Oxide (NOx) – a gas consisting of nitrogen and oxygen; produced during combustion. Emission of most concern in this study.

**Assumptions**

1. All of the power produced by the power take-off shaft was transferred to the hydraulic pump.
2. The biodiesel properties were not altered throughout the time of this study.
3. The data collected is a good representation of continuous engine performance.

**Summary**

The global problem of a dwindling energy supply and the effect of fossil fuel emissions have initiated the need for alternative renewable energy and a more complete understanding of the various components that comprise these renewable energies. It was hypothesized that peanut fatty acid methyl esters from excess peanut production were possible for use in an indirect injection CI engine and that the chemical structure of fatty acid methyl esters affected the fuel properties. It was required to find solutions to issues associated with fuel synthesis, fuel property testing, and engine investigation procedures before the study could be completed. The method of study began with a review of relevant topics and concluded with a full analysis and account of the findings.
Chapter 2

Literature Review

Introduction

Before entering into discussions regarding the details of the research, the past scientific and social events that have helped to shape the biofuels industry were studied. Over the next chapter a review of the history, U.S. policy, transesterification process, fatty acid methyl esters, economics, and combustion of biodiesel will be presented using historical and scientific accounts.

Many years before the development of an engine that would operate using biodiesel. The transesterification of vegetable oil was performed by two scientists, E. Duffy and J. Patrick in 1853.

The first usage of peanut oil in a compression ignition engine was in 1893 in Germany by Rudolph Diesel’s prime model. In remembrance and tribute of this event, August 10 has been considered “International Biodiesel Day” (Meher, Sagar, Naik, 2006).

In 1898 Diesel demonstrated his engine by employing peanut oil and said “The use of vegetable oils for engine fuels may seem insignificant today, but such oils may become in course of time as important as petroleum and the coal tar products of the present time.”

During the 1930’s and World War II, vegetable oils were used as diesel fuels. At the time, countries such as Belgium, Portugal, France, Italy, Brazil, United Kingdom, Germany, Japan, Argentina, and China were known to have tested and used vegetable
oils as diesel fuels. When testing vegetable oils, short term tests were positive. While long term usage of neat vegetable oils or their blends with diesel lead to various engine problems such as injector coking, ring sticking, injector deposits etc. There were high viscosity, low volatility and a tendency to polymerize within the cylinder that were the root cause of many problems associated with direct usage of these oils as fuels (Ma, Hanna, 1999).

A patent was granted of a “procedure for the transformation of vegetable oils for uses as fuels” in 1937 in Belgium to G. Chavanne. This patent explained the process of alcoholysis of vegetable oils using ethanol. According to historians this most likely the first account of “biodiesel” production as it is known today.

Not much was done until the late 1970s and early 1980s, when concerns about high petroleum prices motivated extensive experimentation with fats and oils as alternative fuels (Friedrich, 2004).

Bio-diesel (mono alkyl esters) started to be widely produced in the early 1990s and since then production has been increasing steadily. In the European Union (EU), biodiesel began to be promoted in the 1980s as a means to prevent the decline of rural areas while responding to increasing levels of energy demand. However, it only began to be widely developed in the second half of the 1990s (Dufey, 2006).

The production of biodiesel continues to be modernized and is an area of technology researchers increasingly address due to its appeal as a fossil fuel replacement (Marchetti, Miguel, Errazu, 2005).
U.S. Energy Policy

The need for a change to U.S. energy policy was highlighted by expectations for an ever increasing demand for energy. The transportation sector alone accounts for about 68 percent of the total liquid energy demand, and is expected to rise to 73 percent by 2030. Adding to this need, there is also the expectation that consumption of energy will increase by 20 percent between 2006 and 2030. This increase in energy consumption is due to a predicted relative decrease in energy intensity and increase in population. Total biofuel consumption is predicted to reach 29.7 billion gallons (2.8 quadrillion Btu) by 2030, which represents almost 11.3 percent of total motor vehicle fuel. (Annual Energy Outlook, 2009)

In preparation the Energy Independence and Security Act of 2007 (EISA) is requiring the average fuel economy of new light-duty vehicles (both cars and trucks) to reach 35 miles per gallon by 2020. As well as a 38 percent increase in average fuel economy for in-use stock light-duty vehicles in 2030 compared to 2006 values. (EISA, 2007)

The key legislative action that has spurred on the development of renewable energies in the U.S. is the Energy Policy Act (EPAct). This bill addresses energy utilization and production in the U.S., including: energy efficiency; renewable energy; oil and gas; coal; Tribal energy; nuclear matters and security; vehicles and motor fuels, including ethanol; hydrogen; electricity; energy tax incentives; hydropower and geothermal energy; and climate change technology. (EPAct, 2005)
As a provision of EPAct a tertiary program was created, the Renewable Fuel Standard (RFS1), in 2006. This was the first program in the United States to establish a renewable fuel volume mandate. The program was developed in collaboration with refiners, renewable fuel producers, and stakeholders. The original program, RFS1, required 7.5 billion gallons of renewable fuels to be blended with gasoline by 2012. (RSF1, 2006)

The RSF1 program was later revised by EISA. Key revisions to the program were: inclusion of diesel, in addition to gasoline; increased the volume of renewable fuel required to be blended into transportation fuel from 9 billion gallons in 2008 to 36 billion gallons by 2022; established new categories of renewable fuel, and set separate volume requirements for each one; required EPA to apply lifecycle greenhouse gas performance threshold standards to ensure that each category of renewable fuel emits fewer greenhouse gases that petroleum fuel it replaces. This program laid the foundation for achieving significant reductions of greenhouse gas emissions from the use of renewable fuels, for reducing imported petroleum, and encouraging the development and expansion of our nation's renewable fuels sector. (RSF2, 2007)

**Transesterification**

The most commonly used process is called trans-esterification. The basic process is quite scalable and can be used to produce small or large quantities of biodiesel. The vegetable oils or animal fats are composed of triglyceride molecules that react with the alcohol and catalyst to produce methyl esters, glycerin, some alcohol and some unprocessed waste fat. For process design considerations, the choice of which technology
to use is an economic decision based on the choice of feedstock, the amount of biodiesel to be produced, the desired quality of the finished biodiesel and the co-products produced. While the basic principles of converting all feed stocks into biodiesel are essentially the same, the reactor design and various pretreatment and auxiliary systems will differ according to different feedstocks (Shumaker, 2008).

The basic production processes are transesterification, esterification, and water washing. Water washing is very difficult and should be constantly monitored. There are three feedstocks primary categories: virgin vegetable oils, waste vegetable oils, and rendered animal fats. The favorite feedstock of the very small biodiesel producer is waste vegetable oils from restaurants. The main advantage is the low purchase cost. Palm oil or palm olefin is a feedstock source that may also be used in Georgia under the right location and price conditions. Oil yields using expelling technology will be lower. Typical cold press yields will be about 70 to 75 percent of the total oil content and more advanced heated seed expeller yields may approach 90 percent. For feedstock costs, there were two points to be taken from the potential feedstock prices. One is the general overall upward trends in prices and the second main point was to take from the prices of various biodiesel feedstock is the difference in price between the different potential feedstocks (Shumaker, 2008).

A cold press expeller is basically a screw press that uses mechanical force to press the oil from the seed. This method of obtaining oil requires storage for the oil seeds, a tank and strainer system for the crude oil and storage for the meal product. It is true that the larger the facility, the more it will cost to acquire or build. But it is also generally true
that the capital cost and operating costs per gallon will decline as the size of the facility increases. One major factor in the cost of the larger sized plants deals with the decision on whether or not to process of by-product glycerin and the choice is whether or not to refine the glycerin or just market at as crude product. Smaller plants generally cannot justify the added cost (Shumaker, 2008).

For feedstock issues, the better the feedstock quality the higher the market price and the reverse is true as well. High cost feedstocks make good biodiesel but the cost of the biodiesel is also high. When attempting to use waste vegetable oil one often encounters some problems due to the often high free fatty acid content of the waste vegetable oil. The high free fatty acids, those over 2.5 percent, pose problems for the small biodiesel producer. There are ways of handling the high free fatty acids waste vegetable oil to make them suitable for the small scale biodiesel producer. One way is to dilute them with low free fatty acid oil and another one can also pre-process the high free fatty acid (FFA) oil by adding catalyst and water to change the FFA to soap which can then be removed and this will reduce the volume of the feedstock by the amount of the FFA content (Shumaker, 2008).

In conclusion, while low cost feedstocks appear attractive, they usually need a degree of pre-processing before they are ready to make biodiesel. Pre-processing results in increased costs and lower biodiesel yields from a given amount of feedstock. Also, high quality fuel was less likely to damage engines and helps protect the image of biodiesel as a viable alternative fuel. (Shumaker, 2008)
Biodiesel contains more than 98% FAME. The remaining 2% are antioxidants, free fatty acids, unreacted triglycerides or partially reacted mono or diglycerides, unrecovered methanol, and by-products of transesterification such as glycerol. (Kapila Wadumesthrige, 2008)

Petroleum diesel fuel is a complex mixture of hydrocarbons with carbon atoms ranging from 12 to 18, whereas vegetable oils are mixture of organic compounds ranging from simple straight chain compound to complex structure of proteins and fat-soluble vitamins and are commonly referred as triglycerides. Vegetable oils need to be modified to bring their combustion related properties closer to those of mineral diesel oil because of high viscosity and high flash point due to lower volatility. By taking a triglyceride molecule of a fatty acid and creating ester, it’s called transesterification. For an alkali-catalyzed transesterification, the triglycerides and alcohol must be substantially anhydrous because water makes the reaction partially change to saponification, which produces soap.

The most important variables affecting the yield of biodiesel from transesterification process are: reaction temperature, molar ratio of alcohol to oil, catalyst, reaction time, and presence of moisture and free fatty acids. The rate of reaction is influenced by the reaction temperature, however, the reaction will proceed to near completion even at room temperature. In general, the reaction is conducted close to the boiling point of methanol (60°C to 70°C) at atmospheric pressure. The effect of temperature on conversion of oils and fats into biodiesel has been studied by many researchers. The molar ratio is another variable that affects the yield of ester. The
stoichiometry of the transesterification reaction requires 3 moles of alcohol per mol of triglyceride to yield 3 moles of fatty esters and 1 mol of glycerol. A molar ratio of 6:1 is normally used in industrial processes to obtain methyl ester yields higher than 98% by weight and the ratios greater than 6:1 do not increase yield much, however it interferes with separation of glycerol.

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed and are less corrosive to industrial equipment than acidic catalysts. The effect of reaction time is influenced by the conversion rate that increases with reaction time. Hanna Ma studied the effect of reaction time on transesterification of beef fallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of methanol into beef fallow. Then from one to five minutes, the reaction proceeded very fast. The yield of beef fallow methyl ester surged from 1 to 38%. Water is the example of the effects of moisture and free fatty acids affect the yield. Water causes soap formation, which consumes the catalyst and reduces catalyst efficiency, thus resulting soap causes an increase in viscosity, formation of gels and makes the separation of glycerol difficult.

For the experiment, non-edible vegetable oils such as rice bran, castor, and linseed were obtained from the local market. Transesterification was performed for one hour at 55°C at atmospheric pressure. For esterification in the laboratory, 1 liter of each oil was heated up to 65°C in round bottom flask and stirred vigorously. 5 grams of KOH was dissolved in methyl alcohol in 6:1 molar ratio in a separate vessel and was poured into round bottom flask, while stirring the mixture continuously. Using a Setavis
Kinematic Viscometer, vegetable oils had a higher viscosity compared to diesel oil. Also, viscosity decreases drastically by converting these oils into their esters. The viscosity of linseed, rice bran, and castor oil at 40°C is very high as compared to mineral diesel. Which means high viscosity makes these oils unsuitable for direct use in Compression Ignition engines, but by converting these oils into their methyl esters, it get reduced drastically. (Agarwal, 2004)

Biodiesel is an important new alternative transportation fuel. It can be produced from many vegetable oil or animal fat feedstocks. Conventional processing involves an alkali catalyzed process, but this is unsatisfactory for lower cost high free fatty acid feedstocks due to soap formation. Pretreatment processes using strong acid catalysts have been shown to provide good conversion yields and high-quality final products. These techniques have even been extended to allow biodiesel production from feedstocks like soap stock that are often considered to be waste. (Gerpen, 2005)

Biodiesel is an alternative fuel for diesel engines consisting of the alkyl monoesters of fatty acids from vegetable oils or animal fats. Most of the biodiesel that is currently made uses soybean oil, methanol, and an alkaline catalyst. The high value of soybean oil as a food product makes production of a cost-effective fuel very challenging. However, there are large amounts of low-cost oils and fats such as restaurant waste and animal fats that could be converted to biodiesel. The problem with processing these low-cost oils and fats is that they often contain large amounts of free fatty acids (FFA) that cannot be converted to biodiesel using an alkaline catalyst. In this study, a technique is described to reduce the free fatty acids content of these feedstocks using an acid–
catalyzed pretreatment to esterify the free fatty acids before esterifying the triglycerides with an alkaline catalyst to complete the reaction. Initial process development was performed with synthetic mixtures containing 20% and 40% free fatty acids, prepared using palmitic acid. Process parameters such as the molar ratio of alcohol, type of alcohol, acid catalyst amount, reaction time, and free fatty acids level were investigated to determine the best strategy for converting the free fatty acids to usable esters. The work showed that the acid level of the high free fatty acids feedstocks could be reduced to less than 1% with a 2–step pretreatment reaction. The reaction mixture was allowed to settle between steps so that the water–containing alcohol phase could be removed. The 2–step pretreatment reaction was demonstrated with actual feedstocks, including yellow grease with 12% free fatty acids and brown grease with 33% free fatty acids. After reducing the acid levels of these feedstocks to less than 1%, the transesterification reaction was completed with an alkaline catalyst to produce fuel–grade biodiesel. (Knothe, 2006)

Biodiesel is an alternative diesel fuel that is produced from vegetable oils and animal fats. It consists of the monoalkyl esters formed by a catalyzed reaction of the triglycerides in the oil or fat with a simple monohydric alcohol. The reaction conditions generally involve a trade-off between reaction time and temperature as reaction completeness is the most critical fuel quality parameter. Much of the process complexity originates from contaminants in the feedstock, such as water and free fatty acids, or impurities in the final product, such as methanol, free glycerol, and soap. Processes have
been developed to produce biodiesel from high free fatty acid feedstocks, such as recycled restaurant grease, animal fats, and soap stock (Gerpen, 2005).

A study was performed to investigate the use of low–cost, high FFA feedstocks to produce fuel–quality biodiesel. It was determined that feedstocks with high FFAs could not be transesterified with the traditional alkaline catalysts that have been used with good success for vegetable oils. Alkaline catalysts form soap when they react with the FFAs. Soap removes the catalyst from the reaction and prevents the separation of the glycerin and the ester. A process was developed to use acid catalysts to pretreat the high FFA feedstocks until their FFA level was below 1%, allowing the subsequent use of alkaline catalysts to convert the triglycerides. The effects of the methanol molar ratio, acid catalyst amount, and reaction time on the reduction of FFA level were studied with a simulated high FFA feedstock consisting of 20% palmitic acid in soybean oil. This part of the study showed that the FFA level of the feedstocks could be reduced to less than 1% with a 2–step process of acid–catalyzed pretreatment. Extension of the process to yellow and brown grease showed that higher levels of acid catalyst and methanol were required. The acid–catalyzed pretreatment reaction decreased the acid value of the synthetic mixture to less than 2 mg KOH/g with a 2–step process. Using the 2–step acid catalyzed pretreatment followed by an alkali–catalyzed final reaction, the transesterification reaction was completed in much less time than would be possible with acid–catalyzed transesterification alone. Increasing the acid catalyst amount is very effective in decreasing the acid value of the mixture. In the first pretreatment step, using a 10:1 molar ratio and 30 min of reaction time, the acid value of the simulated high FFA feedstock was
reduced from 41.33 mg KOH/g to 1.37 mg KOH/g using 15% acid catalyst. Ethanol decreased the FFA level of the synthetic mixture faster than methanol. (Knothe, 2006)

When the FFA level is above 5%, the soap inhibits separation of the methyl esters and glycerol and contributes to emulsion formation during the water wash. For these cases, an acid catalyst, such as sulfuric acid, can be used to esterify the free fatty acids to methyl esters.

Freedman compared both crude and refined vegetable oils as feedstocks and found that the yield of methyl esters was reduced from 93% to 98% for the refined oil to 67% to 86% for the crude oil. This was attributed mostly to the presence of up to 6.66% free fatty acids in the crude oil, although phospholipids were also suggested as a source of catalyst destruction. In a study of the effects of phospholipids on biodiesel production, Van Gerpen and Dvorak found that phosphorus compounds in the oil did not carry over into the methyl esters, and while yield was reduced by 3–5% for phosphorus levels above 50 ppm, this was due mostly to added difficulty separating the glycerol from the esters. (Gerpen, 2005)

Transesterification of four vegetable oils; canola oil, green seed canola oil from heat-damaged seeds, processed waste fryer grease and unprocessed waste fryer grease, was carried out using methanol, and KOH as catalyst. The methyl esters of the corresponding oils were separated from the crude glycerol, purified, and characterized by various methods to evaluate their densities, viscosities, iodine values, acid numbers, cloud points, pour points and gross heat of combustion, fatty acid and lipid compositions, lubricity properties, and thermal properties. The fatty acid composition suggests that 80–
85% of the ester was from unsaturated acids. Substantial decrease in density and viscosity of the methyl esters compared to their corresponding oils suggested that the oils were in their mono or diglycerides form. (S.L. Dmytryshyn a, 2004)

From the analysis performed it is determined that all four types of oils can be used to produce biodiesel. Overall, the best ester yield relative to the theoretical yield was the canola methyl ester. The green seed methyl ester had a yield that was also satisfactory. Both the canola methyl ester and the green seed methyl ester had similar physicochemical properties, which compared well to diesel fuel. Due to a low LN, the green seed methyl ester does not compare well to diesel fuel, and should not be used as an additive until further modifications to the production procedure are performed. Therefore, from the four methyl esters produced, the best choice to use as a fuel or as an additive would be the canola methyl ester. (S.L. Dmytryshyn a, 2004)

Following the reaction during the process of transesterification, the glycerol is removed from the methyl esters. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly and may be accomplished with either a settling tank or a centrifuge. The excess methanol tends to act as a solubilizer and can slow the separation. However, this excess methanol is usually not removed from the reaction stream until after the glycerol and methyl esters are separated due to concern about reversing the transesterification reaction. Water may be added to the reaction mixture after the transesterification is complete to improve the separation of glycerol. (Gerpen, 2005)
The first step in refining the glycerol is usually to add acid to split the soaps into free fatty acids and salts. The free fatty acids are not soluble in the glycerol and will rise to the top where they can be removed and recycled. The salts remain with the glycerol although depending on the chemical compounds present, some may precipitate out. One frequently touted option is to use potassium hydroxide as the reaction catalyst and phosphoric acid for neutralization so that the salt formed is potassium phosphate, which can be used for fertilizer. After acidulation and separation of the free fatty acids, the methanol in the glycerol is removed by a vacuum flash process or another type of evaporator. At this point, the glycerol should have a purity of approximately 85% and is typically sold to a glycerol refiner. The glycerol refining process takes the purity up to 99.5% to 99.7% using vacuum distillation or ion exchange processes. The methanol that is removed from the methyl ester and glycerol streams will tend to collect any water that may have entered the process. This water should be removed in a distillation column before the methanol is returned to the process. (Gerpen, 2005)

While virtually all commercial biodiesel producers use an alkali-catalyzed process for the transesterification process, other approaches have been proposed, including acid catalysis and enzymes. The use of acid catalysts has been found to be useful for pretreating high free fatty acid feedstocks to convert the FFAs to esters but the reaction rates for converting triglycerides to methyl esters are too slow. (Gerpen, 2005)

Fuel quality issues are commonly reflected in the contaminants or other minor components of biodiesel. This work categorizes both the restricted species in biodiesel
and the physical property prescribed by the standards, and details the standard reference methods to determine them as well as other procedures. Other aspects of biodiesel analysis, including production monitoring and assessing biodiesel/petrodiesel blends are also addressed. The types of analyses include chromatographic, spectroscopic, physical properties-based and wet chemical methods. The justifications for specifications in standards are also addressed. (M. Canakci, 2001)

Biodiesel properties may be enhanced by additives. In order to provide acceptable cold flow properties, biodiesel is generally produced from feedstock that contains substantial amounts of unsaturated fatty acids (Gerpen, Biodiesel Production, 2007).

Biodiesel can also be used as heating oil. Accordingly, a separate standard (EN 14213) exists in Europe for biodiesel that is to be used as heating oil. The specifications of EN 14213 are also contained in Table 2. (M. Canakci, 2001)

**Fatty Acid Methyl Esters**

Biodiesel is an alternative diesel fuel derived from the transesterification of vegetable oils (or other triacylglycerol comprised materials such as animal fats or waste frying oils) with simple alcohols to give the corresponding mono-alkyl esters. The cetane numbers of these esters are not significantly affected by branching in the alcohol moiety. Branched esters improve the cold-flow properties of biodiesel and can be employed without greatly influencing ignition properties compared to the more common methyl esters.
Bio-oils (or vegetable oils) contain fatty acids, carboxylic acids that have long, unbranched chains that are either saturated or unsaturated. They also have the ability to react with alcohols that produce esters of the fatty acids, which is important in the transesterification process. The fatty acids that were investigated are oleic, linoleic, linolenic, stearic, and palmitic. Fatty acids derived from natural fats and oils commonly have a chain of 4 to 28 carbons and are usually even numbered. If a fatty acid is saturated, it contains double bonds. The next two carbon atoms in the chain that are bound to either side of the double bond can occur in a cis or trans. A cis configuration means that adjacent hydrogen atoms are on the same side of the double bond. The rigidity of the double bond freezes its conformation and causes the chain to bend and restricts the conformational freedom of the fatty acid. This can be seen in the molecular structure of oleic, linoleic, and linolenic acid. A trans configuration means that the next two hydrogen atoms are bound to opposite sides of the double bond. They do not cause the chain to bend much and their shape resembles a straight, saturated fatty acid. If a fatty acid is saturated, it usually has 12 to 24 carbon atoms that have no double bonds and is saturated with hydrogen. This can be seen in palmitic and stearic acid. The properties of the fatty methyl esters that make up the composition of the biodiesel determine the fuel properties of the biodiesel. The properties of these fatty methyl esters are based on the structure of the fatty acid. The composition of the FAME in the biodiesel is primarily affected by the identity of the source of the fat or vegetable oil. The exact identity of the mixture of fatty esters affects the characteristics of the biodiesel. The carboxylic acids vary in identity based on two main factors, the length of their carbon tails and the degrees of saturation.
within the tail. These properties determining chemical identity have other implications in regards to their resulting FAME/biodiesel such as; combustibility, viscosity, cloud point, and heat output. A fuel property that is important for low temperature operation of diesel fuel is cloud point. Cloud point is the temperature at which a cloud of wax crystals first appear in a liquid when it is cooled and an indication of the lowest temperature at which the fuel can operate. It’s a crucial factor in the cold weather performance of biodiesel fuels; biodiesel fuels typically have higher cloud points than standard diesel fuel. Operating temperatures below the cloud point for diesel fuel can result in fuel filter clogging. Higher saturation in oils tends to lead to biodiesel fuels with higher cloud points. This is based on the fact that saturated fatty acids freeze at higher temperatures than unsaturated fatty acids.

Reid, Prausnitz and Poling (1987) show how chemical structure can be used to compute properties for pure components. They also discuss mixing rules to estimate properties for mixtures. Many such properties are directly measured by chemical analysis, or are calculated by knowing the ester composition in the fuel. In particular, the kinematic viscosity, cetane number, and cloud point of the fuel are dependent on the ester composition. In the formulation of biodiesel, the chemistry of the components is well defined. Since the fuel is an ester of fatty acids derived from natural sources, the main fatty acids normally present in considerable quantity are palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid and erucic acid. The fatty acid profile of biodiesel is identical to that of the parent oil or fat while the composition changes by feedstock, but the components do not. The most common fatty esters contained in biodiesel are
therefore; palmitic (hexadecanoic) acid, stearic (octadecanoic) acid, oleic (9(Z)-octadecenoic) acid, linoleic (9(Z),12(Z)-octadecadienoic) acid, and linolenic (9(Z),12(Z),15(Z)-octadecatrienoic) acid. This composition holds true for biodiesel feedstock, such as soybean, sunflower, rapeseed (as canola), palm, and peanut oils. The canola and green seed methyl esters did not freeze until 50 ºC, but the processed and unprocessed grease methyl esters began freezing at around 10 ºC. Therefore, in regions with a cold climate, processed and unprocessed grease methyl esters would be a poor choice to use as a transportation fuel source. (S.L. Dmytryshyn a, 2004)

Biodiesel is a domestic and renewable alternative with the potential to replace some of the petrodiesel market. An essential feature of biodiesel is that its fatty acid composition corresponds to that of its parent oil or fat, which biodiesel fuels derived from different sources, can have significantly varying fatty acid profiles and properties. The most common fatty esters contained in biodiesel are those of palmitic acid, stearic acid, oleic acid, linolenic acid and linoleic acid. This holds for biodiesel feedstocks, such as soybean, sunflower, rapeseed (as canola), palm, and peanut oils. (Gerhard Knothe, 2003)

The fatty acid composition of biodiesel greatly influences its cold-flow properties. The freezing point of a biodiesel fuel increases with increasing carbon atoms in the carbon chain and decreases with increasing double bonds. According to this knowledge, it is an expected result that the biodiesel from feedstocks with large amounts of saturated fatty acids have higher cloud points and pour points. As a matter of fact, vegetable oil based biodiesel has lower cloud and pour point than that of the biodiesel from fats and greases (M. Canakci, 2008).
Each of the other three methyl esters contains a small amount of triglycerides indicating that esterification in these cases was slower than that in the case of canola oil. The canola methyl ester had the lowest viscosity. The heat of combustion of the methyl esters was slightly lower than their respective oils and waste fryer greases, except for the canola methyl ester, which was similar. The canola methyl ester had the lowest cloud point and the unprocessed waste fryer grease methyl ester had the highest. The canola and green seed methyl esters had relatively lower pour points than the processed and unprocessed waste fryer grease methyl esters. The pour points for the diesel fuel was much lower than those of processed and unprocessed waste fryer grease methyl esters and was somewhat lower than those of the canola and green seed methyl esters. (S.L. Dmytryshyn a, 2004)

The lubricity of the methyl esters, when blended at 1% (vol.) treat rate with ISOPAR M reference fuel, showed that the canola methyl ester enhanced the fuel’s lubricity number. From the analyses performed, it was determined that the ester with the most potential for being an additive or a substitute for diesel fuel is the canola methyl ester, whose physical and chemical characteristics are similar to diesel fuel. (S.L. Dmytryshyn a, 2004)

It has been reported that biodiesel derived from various feedstocks has a CN range of 48-67, mainly depending on the fatty acid composition of the base oil but also on several parameters such as oil processing technology and climate conditions where vegetable oil is collected. (A. S. Ramadas, 2006)
With increasing chain length, decreasing branching and unsaturation, cetane number increases. These chemical structures increase the heating value as well, so there is a tendency for cetane number to increase with viscosity and heating value. (M. Canakci, 2008)

The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN. The CN of biodiesel from animal fats is higher than those of vegetable oils. (Bala, 2005)

The degree of saturation, chain length and branching of the fatty compounds will influence the CN to varying degrees. A study by Knothe reported that CN would generally increase as larger branched esters are produced from different alcohols of increasing chain length. (G. Knothe, 2003)

The location(s) of the double bond within FAMEs will also influence the CN. Szybist altered the fatty acid compulsion of soy-derived fuels by increasing the methyl oleate (C18:1) from 23 to 76% while decreasing the methyl linoleate (C18:2) from 52.1 to 6.7% to achieve a very modest increase of the DCN from 48.2 to 50.4. (J. Szybist, 2005)

Effect of Ester Oxidation

There are few reports on the variation of cetane number of biodiesel with aging and the composition change during aging. And no correlation has been given with FAME composition, oxidative time and cetane number. (Kapila Wadumesthrige, 2008) Fatty acid oxidation is a complex process that occurs via formation of hydro peroxides. (Kapila Wadumesthrige, 2008)
The fatty acid composition of the oils seems to have an important role in the performance of the biodiesel in diesel engine (Dorado et al., 2004). Based on the fatty acid composition and many other parameters, the EU biodiesel specifications will be mandatory to limit the oxidative stability, as it may be a crucial parameter for injection pump performance. The fatty acid composition of the biodiesel samples was determined by gas chromatography after preparation of fatty acid esters according to the Hartman & Lago (1973) method. (Ferrari, Oliveira, Scabio, 2005) The duration of the induction period is a measure of its resistance to oxidation. The most significant and undesirable instability change in liquid fuel with time is the formation of solids, also termed filterable sediments (Mushrush et al., 2001a). During long-term storage, oxidation due to contact with air (autoxidation) presents a legitimate concern with respect to maintaining fuel biodiesel quality. (Ferrari, Oliveira, Scabio, 2005) The objective of this work was to determine the oxidative stability of biodiesel produced by ethanolysis of neutralized, refined, soybean frying oil waste, and partially hydrogenated soybean frying oil waste. The evaluation was conducted by means of the Rancimat equipment, at temperatures of 100 and 105 °C, with an air flow of 20 L/hr. The fatty acid composition was determined by GC and the iodine value was calculated. It was observed that even though the neutralized, refined and waste frying soybean oils presented close comparable iodine values, biodiesel presented different oxidative stabilities. The biodiesel from neutralized soybean oil presented greater stability, followed by the refined and the frying waste. Due to the natural antioxidants in its composition, the neutralized soybean oil promoted a larger oxidative stability of the produced biodiesel. During the deodorization process, the
vegetable oils lose part of these antioxidants; therefore the biodiesel from refined soybean oil presented a reduced stability. The thermal process degrades the antioxidants, thus the biodiesel from frying waste oil resulted in lower stability, the same occurring with the biodiesel from partially hydrogenated waste oil, even though having lower iodine values than the other. (Ferrari, Oliveira, Scabio, 2005)

When oxidation occurs at ordinary temperatures, the initial products are hydro peroxides. As the oxidation continues, the peroxides may split and form aldehydes, ketones and short chain acids that produce unpleasant odors. Oxidation eventually deteriorates the fuel properties because of gum formation. This formed gum does not combust completely, resulting in carbon deposits in the combustion chamber and lubrication oil thickening. Moreover, as it oxidizes, biodiesel becomes more viscous and its cetane number raises. Therefore, the oxidized biodiesel starts to burn earlier than an unoxidized biodiesel, which causes NOx emission to increase. The chemical structure of biodiesel fuel is an important factor in the oxidation reaction. Oxidation is caused from the presence of double bonds in the chains, that is, feedstocks rich in polyunsaturated fatty acids are much more susceptible to oxidation than the feedstocks rich in saturated or monounsaturated fatty acids. For instance, relative rates of oxidation are 1 for oleates, 41 for linoleates and 98 for linolenates. The methyl esters oxidized at different rates but appeared to reach a single maximum peroxide value of 300–350 meq/kg ester. The corn oil methyl ester might also follow this pattern but the test duration of 240 h was reached before the corn oil had oxidized to this level. The methyl esters of oils that are less saturated tend to have higher rates of oxidation. (M. Canakci, 2008)
Among these components aldehydes may contribute to a higher cetane number, based on the results of NREL report on cetane number of several compounds. The decrease in unsaturation number during oxidation also suggests the formation of polymeric materials. (Kapila Wadumesthrige, 2008) The very high DCN of these ambient oxidized samples compared to 110C accelerated oxidation samples are due to the collective effect of primary oxidative products (hydro peroxides) and secondary oxidation products such as aldehydes, carboxylic acids and polymers of FAME. (Kapila Wadumesthrige, 2008) The C18:2 compositions decreased from 53 to 12.6% within 4 months. The rest of the cetane number increase is due to the formation of oxidative products from FAME. (Kapila Wadumesthrige, 2008)

The highly saturated fatty acid level in fact proves to be advantageous in terms of storage stability as compared to the more unsaturated vegetable oil-based fuels, which are more susceptible to the chemical deterioration (e.g. autoxidation and polymerization) under certain conditions of storage temperature, moisture, ultraviolet radiation, and packaging materials (Wu et al., 1998). The results obtained for partially hydrogenated frying oil waste showed that it has greater percentage of unsaturated acids in its composition and it also presented lower iodine value, which should have provided a higher oxidative stability. However, when the partially hydrogenated frying oil waste was used for transesterification, the biodiesel obtained did not present a good stability probably because of the frying process to which it was submitted previously. Methyl esters performed slightly better than ethyl esters during the storage test in stability studies carried by Du Plessis et al. (1985). (Ferrari, Oliveira, Scabio, 2005)
The biodiesel from neutralized soybean oil presented greater oxidative stability maybe due the presence of natural antioxidants in its composition. The biodiesel from refined soybean oil, due to the deodorization process, when part of these antioxidants are lost, presented less stability. Due to the thermal process which degrades antioxidants present in the oil, biodiesel from soybean frying oil waste showed lower stability. Biodiesel produced from partially hydrogenated frying oil waste, even though it possessed low iodine value in comparison to the other, presented low oxidative stability possibly due to the thermal process to which it was submitted previously. (Ferrari, Oliveira, Scabio, 2005) The biodiesel from neutralized soybean oil presented greater stability, followed by biodiesel from refined and from frying waste. This can be explained by the fact that the neutralized soybean oil has in its composition natural antioxidants, as for example tocopherol (Hartman & Esteves, 1981), which increases the stability of the oil and also shows beneficial effects on retarding oxidative degradation of biodiesel produced from this oil. Otherwise, the refined soybean oil, because of the refining process, mainly in the stage of the deodorization, loses part of its natural antioxidants, which also decreases the stability of the biodiesel. (Ferrari, Oliveira, Scabio, 2005)

**Economics of Biodiesel Synthesis**

The introduction of bio-diesel could stimulate the economy while at the same time offer reduced dependence on a diminishing energy source (fossil fuels). As the interest grows in the product it will start to become accepted more and more and rise exponentially until it has majority market share. The inevitable fluctuation of gas price is
something that cannot be controlled. If biodiesel were introduced into the mainstream market, dependence on foreign countries would diminish. Bio-fuels could serve as a means to reinvigorate the faltering U.S. economy over the next few years, according to a new report focused on the economics of biotechnology (Grant, 2009). Conversion to bio-fuels could result in the following advantages:

- Direct job creation from advanced bio-fuels production could reach
  29,000 by 2012, 94,000 by 2016, and 190,000 by 2022.
- Total job creation, accounting for economic multiplier effects, could reach 123,000 in 2012, 383,000 in 2016, and 807,000 by 2022.
- Direct economic output from the advanced bio-fuels industry is estimated to rise to $5.5 billion in 2012, $17.4 billion in 2016, and $37 billion by 2022.
- Taking into consideration the indirect and induced economic effects, the total economic output effect for the U.S. economy is estimated to be $20.2 billion in 2012, $64.2 billion in 2016, and $148.7 billion in 2022.
- Advanced bio-fuels production under the RFS could reduce U.S. petroleum imports by approximately $5.5 billion in 2012, $23 billion in 2016, and nearly $70 billion by 2022.
- The cumulative total of avoided petroleum imports over the period 2010–2022 would exceed $350 billion (Grant, 2009).

“Increasing advanced bio-fuel production to a modest target of 45 billion gallons by 2030, which can be achieved by maintaining the same pace of technology development, could create more than 400,000 jobs within the industry and 1.9 million new jobs
throughout the economy. Further, it could provide an economic boost of $300 billion. Continued federal support can help the industry quicken the development of the necessary technology and weather the risk of oil price volatility.” (Bio-era, 2009)

One of the more popular areas for research is the introduction of different materials to make biodiesels. Bio-diesel can be made from almost twenty-five different types of vegetable oil and animal fat deposits, although considerable debate exist over which methods are the most efficient. One of the most common types of precursors that are used to make bio-diesel is cooking oil. Cooking oil can be reused and refined to make bio-diesel. There is still a lot of confusion and controversy surrounding the differences between waste vegetable oil (WVO) and pure vegetable oil grown specifically for fuel, SVO (Straight Vegetable Oil). Waste vegetable oil goes through a process of cleaning, transesterification, and refining that shortens the lipid chains, before it is used as fuel. Once processed, certain diesel engines can run on 100 percent blends of this biodiesel with no engine adjustments or mixes with mineral diesel needed (Van Gerpen, 2004). One of the benefits of using biodiesel made from waste vegetable oil is in utilizing a waste product, which until recently has been poured down drains or sent to a landfill. According to research by the BBC, the catering industry in the UK produces about 50-90 million liters of waste cooking oil each year, while Ireland discards more than 10,000 tons of waste vegetable oil annually (Van Gerpen, 2004) all of which have the potential to be used in biodiesel production. Although this sounds like a significant amount of oil, there is simply not enough cooking oil in the UK to entirely replace petroleum diesel needs. This estimate is based on a report by the Government's Better Regulation
Commission. Current waste oil supplies could only feasibly power around one out of every three hundred fifty of the UK's cars. In fact, the Energy Systems Research Unit estimates that the UK can only produce enough bio-diesel from waste vegetable oil to displace less than 0.6% of conventional diesel engines (Patel et al, 2003).

Biofuels that are termed second-generation biofuels are also a productive opportunity for clean energy. Second generation biofuels are derived from lingo cellulose crops. Plants are made from lignin and cellulose, second generation biofuels extract these two components of these plants and split them. After this process the cellulose is fermented into alcohol in much the same way as first generation biofuels. Second generation bio-fuel technologies have been developed because first generation biofuel manufacturing has certain limitations that is mainly a threshold above which they cannot produce enough biofuel without threatening food supplies and biodiversity. Second generation biofuels can help solve such problems and can supply a larger proportion of fuel supply sustainably, affordably, and with greater environmental benefits (Grant, 2009). Second-generation biofuels include cellulosic ethanol, which is made from plant waste such as wood chips or straw. Such products are currently considered less controversial than first-generation biofuels, which have been linked to food price inflation, deforestation and a questionable performance in terms of reducing carbon emissions (Mosier et al, 2003).

Energy consumption and modes of energy production have a direct as well as an indirect effect on the economy. Everything consumed must be transported from some remote location. If the cost of gas is low, then it costs less to transport these materials,
resulting in a lower cost for the consumer. Lower fuel cost on the other hand translates into substantially lower prices down the supply chain. This is attributable primarily to lower transportation costs. If the price of gas rises, then so does the price of all transported goods. It can thus be appreciated that gas prices and consequently energy prices constitute a major force in driving the economy. Development of a fuel with reliable and predictable supply characteristics would result in a more predictable economy compared to the current petroleum prices which are very unpredictable and unstable.

Advancements in bio-diesel technologies are the driving force behind creating a strong market for bio-diesel and other bio-fuels. Creating a manufacturing process that would cut cost by as little as 5 or 10 percent would cause bio-diesel production cost to drop below the cost of petroleum and make it more reasonable for most consumers to choose bio-diesel over petroleum based fuels. Minute changes could have dramatic effects that could help skew prices and production in the right direction. Petroleum gas prices have been increasing. Bio-fuel sources are more plentiful thus, their prices are more sustainable and predictable (NCEP, 2004).

After the need for supply is determined, a cost conscious method of production is needed to make it commercially available at a reasonable cost. The concern with new technologies is that as the cost of production and profit margins increase the product cost is far higher than it’s worth. Since petroleum based fuels have been around for such a long time, its production process has nearly been perfected and the idea of a new fuel and new ways to produce and manufacture it are expensive and possibly unreasonable. Even
when the general public is unwilling to change their consumption habits substantially, especially in the face of high cost related to the change, with the unpredictable but constant rise in gas prices, it is inevitable that the price of both fuels will be more compatible as the limitation of natural resources causes the price of fossil fuels to rise until it is cost efficient to use renewable fuels. The support of these methods now can preserve resources and cut cost today and in the future.

Once the technology can be developed within reason it must then be tested for both quality and safety. Numerous trials must be conducted including failure testing, statistical analysis, wear and tolerance analysis, stress analysis, and environmental reactions to the product especially those dealing with fuels that cause emissions of toxic chemicals and particles. Burning of fuel causes indirect and long-term effect on the engine and the environment. These different variables must be manipulated and results analyzed before any type of mass production could begin. Most biofuels are environmentally friendly and release little to no harmful emissions. As for biodiesel, it produces 50% less CO\textsubscript{2} and zero SO but in turn produces 10% more nitrogen oxide than convention diesel. Nitrogen oxide emissions can be reduced with the use of a catalytic converter, thus making it more efficient and more economically viable than petroleum based fuels (Van Gerpen, 2004).

In order to make the aforementioned technologies commercially available, a method must be found that distinguishes issues that are preventing mass production and consumption. It can be recognized that the first challenge is acceptance within the market. If the technology is not accepted it does not need to be produced. Preparation for
conversion is not necessary and neither is any other significant measure to prepare for the change from the current technology. Once the technology is accepted and the consumers develop a demand for the product. It can then become feasible to create a supply to accompany the demand. To do this an adequate amount of testing and development needs to be done in order to ensure the product is safe and serves its purpose without any undesirable effects (Van Gerpen, 2004).

As Georgia is by far the largest producer of peanuts in the U.S. (about 50% of total U.S. production comes from Georgia), the market of rejected peanuts could help to stimulate economic recovery that is drastically needed at this point. Advantages of using peanut oil for biodiesel production include a significant increase in yield when compared to the most widely used U.S. biodiesel feedstock, the soybean. On the engine side it is reported that peanut biodiesel will clean residue from a fueling system of the diesel engine, while providing an increased lubricity helping to offset a decrease in mechanical efficiency from the ultra-low sulfur content diesel, as well as a significant reduction in both particulate matter and sulfur-oxide emissions.

Bio-fuels can also be created from vegetable oils, animal fats, and recycled grease composites; this is called bio-diesel. Last year biofuels provided almost 2% of the world’s transport fuel (Vanudevan, 2008).

Based on data from the Energy Information Administration, in 2004 over 1.9 billion gallons of diesel fuel oil was consumed in Georgia for various purposes. A B2 blend into that stream would require over 38 million gallons and a B20 blend would use over 384 million gallons. It is clear there is a broad market with great potential for
biodiesel use in Georgia. The study examined five different plant sizes: 5, 10, 15, 30, and 60 million gallon per year plants. The 5 million gallon per year plant has the highest cost of production and the 60 million gallon per year has the lowest cost of production, but only 6 cents per gallon less than the 10 million gallon per year plant.

There were some benefits for biodiesel like the implementation of biodiesel into the nation’s diesel fleets of trucks, tractors, power engines and passenger vehicles can be accomplished in a relatively seamless manner, particularly when used at a low percentage blend. It can be blended into petro diesel simply by pouring the two liquids together, called splash blending. Current biodiesel production happened in the fall of 2006, and there were 67 commercial sized biodiesel production facilities actively making and selling biodiesel in the US. The total estimated current production capacity in the three state area (Georgia, Alabama, Tennessee) is about 20.5 million gallons but would rise to over 80 million gallons with the proposed Columbus plant that is being planned.

There are two basic biodiesel technologies that are commonly in use: transesterification and esterification. Given the choice made for the basic production process, the next decision concerns how the plant will actually be operated and there are three basic options: batch, continuous, or batch-continuous. Batch operations are conducted in discreet units. A continuous operation is the process of an ongoing flow of feedstocks, reactions and purification. Batch-continuous is the attempt to reap the benefits of both of the above processes as it adapts characteristics of both. Then the product proceeds to the purification stage and there are four primary methods: water washing, active filtration, ion exchange, and fractional distillation.
Total revenue in Georgia for economic impact of biodiesel, is the direct output of the operation and is projected as $88.6 million from biodiesel sales and sales of glycerin as a byproduct. Economic activity related to construction generates $6.5 million in labor income for 178 jobs and production of biodiesel creates annual economic output impacts of $181.5 million. Plant operations account for 24.5% of the total output impact, while 75.5% of the output impact is attributable to soybean oil from soybeans produced in Georgia. Biodiesel production generates $3.3 million for the state treasury and $2.7 million for local governments in the state.

The purpose of this report’s study was to update projected cost for biomass resources produced in Georgia that could be available for producing energy. The Center for Agribusiness and Economic Development (CAED) initially evaluated the potential of utilizing Georgia’s biomass resources to produce energy in 2003 and has updated the study in 2007. In 2003, the CAED completed their study of the feasibility of generating electricity from biomass fuel sources in Georgia. The results from the study indicated that it was not economically feasible to produce electricity with the technologies available at that time without significant subsidies.

Georgia has a large amount of potential biomass feedstocks available for conversion into energy. The properties and characteristics of each potential bio-fuel have important implications to the feasibility of individual biomass sources. In order to optimize feasibility, feedstocks must provide generators with an abundant supply at the lowest cost of delivery possible. Biomass sources differ in ash and moisture content and this affects the energy value of biofuels, since the chemical make-up of ash generally has
no energy value and the amount of water in bio-fuel affects, in a decisive manner, the available energy within every bio-fuel.

The CAED amassed data concerning the sources and costs of providing biomass for the conversion to energy process and evaluated the economics cost involved. Different potential feedstocks will have vastly different delivered costs per ton due to both the current market price of the product and its relative cost of transportation or unit. Since generation of electricity in a minute to minute operation, an assurance of a continuous supply of feedstock is very important. Factors to consider are moisture content and ash content. High moisture content implies high drying costs that can add to the total cost of electricity production and high ash content feedstocks require added boiler design considerations that raise capital costs.

Corn stalk in Georgia based on the 2005 Farmgate data was 164,570 for the estimated production. For cotton stalks production, the total 2005 Farmgate acreage was multiplied by the estimated pounds of stalk available per acre and the total estimated cotton stalks produced are 2.72 million tons. Gin trash is another potential biomass source produced in Georgia, it is estimated that every bale of cotton ginned produces 185 pounds of gin trash.

Peanut hay is estimated that each acre of peanut produces between 3 and 4 bales of peanut hay weighing 1,200 pounds per bale. Baling hay is a relatively inexpensive venture and a market exists for hay. For peanut hulls, the total tons available were estimated by taking 25% of the total production and hulls comprise approximately 25% of the weight of peanuts. On the hand, pecan hulls were estimated by the tons available as
well, but the total production was multiplied by the typical shelling rate (33%) and the average percentage of hulls (51%). The best way to load pecan hulls would be mechanically.

In certain years hay production in Georgia is in excess of consumption and given recent droughts, cattle prices, and growing equine industry in Georgia, hay may not be a consistent form of biomass. Based on 2005 Farmgate data, the estimated tons of hay available would be 674,811. Wheat and rye straw each produce 110 to 120 square bales per acre weighing around 30 pounds per bale. Georgia would produce 366,834 tons of wheat straw and 139,993 tons of rye straw. Poultry products such as poultry litter, which is the poultry and egg industry, is the most valuable agricultural sector of Georgia and leads the nation in poultry production. For forest related products, the three primary sources of forest residue that was considered in the study were bark, wood chips, and wood (harvesting) residues.

The purpose of this report was to provide decision makers with information on the feasibility of producing biodiesel in Georgia. The state of Georgia faces two issues that may provide a unique opportunity for rural economic growth. The first issue is major urban areas of the State have air quality problems that will require actions to reduce sources of pollution. The second issue is depressed crop farm incomes due to low market prices for the many oilseeds produced.

Major feedstocks for the methyl ester process currently available in Georgia include soybean oil, cottonseed oil, peanut oil, spent restaurant fats and rendered poultry fats. Poultry is the leading agricultural commodity in the state and the volume of boiler
fat produced in Georgia is high. Another potential feedstock is spent fats or yellow grease. Yellow grease is inedible fat, oil and grease used and removed from the food service industry. Most of the yellow grease produced in Georgia is collected by renderers who clean the grease and prepare it for other use in chemicals, soap, cosmetics, plastics, lubricants, and livestock and poultry feeds.

The feedstock needed to run at full capacity ranged from 3.75 million pounds at the smallest level of production to 225 million pounds at the highest level of production. The physical plant would require approximately 7 to 10 acres for the building, tank farm and transportation areas. The building needed to house the plant would be approximately 5,000 square feet and about 60 feet in height. Feedstock costs represent between 50 and 75 percent of the cost of producing biodiesel and thus reliable source of low priced feedstocks is critical to success.

**Combustion and Emissions of Biodiesel**

Scientific research confirms that biodiesel exhaust is less harmful to humans than diesel fuel exhaust because it lacks aromatic compounds. The purer the biodiesel fuel is, the less likely it is to create the cancer causing compounds polycyclic aromatic hydrocarbons. Most of the poisonous compounds common to diesel exhaust are reduced by 75 to 85 percent by using bio-diesel fuel (Lindhjem et al, 2003). Biodiesel is also easier on the lungs because it reduces the emission of particulate matter that causes asthma and other lung disorders by about 47%. Burning just a 2% biodiesel blend in on-road vehicle that usually takes diesel fuel will cut harmful emissions but significant advantages are not realized until a blend of 20% is employed. Annually this one action
has the potential to reduce poisonous carbon monoxide emissions by more than 35 million pounds, reduce ozone forming hydrocarbon emissions by almost 4 million pounds, reduce hazardous diesel particulate emissions by almost 3 million pounds and reduce acid rain-causing sulfur dioxide emissions by more than 3 million pounds (Lindhjem et al, 2003). It is obvious that increased bio-diesel use would result in a cleaner environment. Emission of harmful chemicals into the atmosphere such as hydrocarbons, carbon monoxide and other harmful chemicals and particle matter from burning biodiesel are significantly less than those of petroleum based diesel emissions. The only toxin more harmful than petroleum diesel in bio-diesel emissions is nitrous oxide. It will be appreciated that emissions in the form of particulate matter (PM), carbon monoxide (CO), and sulfur oxides (SOx) are reduced substantially as the amount of bio-diesel in any fuel combination approaches 100 %. It will also be noticed that the only noteworthy change in emissions results with a small increase in nitrogen oxide (NOx) concentration.

Exhaust from conventional fueled diesel vehicles contains numerous known and suspected human carcinogens. Diesel exhaust was recently classified as a Toxic Air Contaminant by the California Air Resources Board (Van Gerpen, 2004); was the subject of an EPA health risk assessment (EPA, 2010), and a critical review by the Health Effects Institute (1995), which is sponsoring on-going work in this area. One of the potential benefits of biodiesel fuel use is a decrease in the overall toxicity of emissions. This is a result of the elimination or reduction of certain toxic components of diesel exhaust, which are present in conventional fuels but not in biodiesel. Additional benefits may be associated with potential reductions in the total mass of particulate matter in the exhaust.
Biodiesel has been shown to have multiple benefits to the environment when it is compared to petroleum-based fuels. Particulate emissions are reduced by around 50 percent compared with fossil-sourced diesel. Also carbon intensity of biodiesels is sufficiently less than that of petroleum diesels (Lindhjem et al, 2003).

Substituting 100% biodiesel (B100) for petroleum diesel in buses reduces the life cycle consumption of petroleum by 95%. This benefit is proportionate with the blend level of biodiesel used. When a 20% blend of biodiesel with petroleum diesel (B20) is used as a substitute for 100% petroleum diesel in urban buses, the life cycle consumption of petroleum drops 19%. (John Sheehan, 1998)

Biodiesel yields 3.2 units of fuel product energy for every unit of fossil energy consumed in its life cycle. The production of B20 yields 0.98 units of fuel product energy for every unit of fossil energy consumed. By contrast, petroleum diesel’s life cycle yields only 0.83 units of fuel product energy per unit of fossil energy consumed. Such measures confirm the “renewable” nature of biodiesel. (John Sheehan, 1998)

Biodiesel reduces net emissions of CO$_2$ by 78.45% compared to petroleum diesel. For B20, CO$_2$ emissions from urban buses drop 15.66%. (John Sheehan, 1998)

The use of B100 in urban buses results in substantial reductions in life cycle emissions of total particulate matter, carbon monoxide and sulfur oxides (32%, 35% and 8% reductions, respectively, relative to petroleum diesel’s life cycle). (John Sheehan, 1998)

Tailpipe emissions of particulates less than 10 microns in size are 68% lower for buses run on biodiesel (compared to petroleum diesel). In addition, tailpipe emissions of
carbon monoxide are 46% lower for buses run on biodiesel (compared to petroleum diesel). Biodiesel completely eliminates emissions of sulfur oxides at the tailpipe. (John Sheehan, 1998)

The use of B100 in urban buses increases life cycle emissions of NOx by 13.35%. Blending biodiesel with petroleum proportionately lowers NOx emission. B20 exhibits a 2.67% increase in life cycle emissions of NOx. Most of this increase is directly attributable to increases in tailpipe emissions of NOx. B100, for example, increases tailpipe levels of NOx by 8.89%. (John Sheehan, 1998)

Total life cycle emissions of hydrocarbons are 35% higher for B100, compared to petroleum diesel. However, emissions of hydrocarbons at the tailpipe are actually 37% lower. The increase in hydrocarbon emissions is due to release of hexane in the processing of soybeans and volatilization of agrochemicals applied on the farm. (John Sheehan, 1998)

One MJ of biodiesel requires an input of 1.2414 MJ of primary energy, resulting in a life cycle energy efficiency of 80.55%. Biodiesel is comparable to petroleum diesel in the conversion of primary energy to fuel product energy (80.55% versus 83.28%). (John Sheehan, 1998)

A fumigation system injects a gaseous or liquid fuel into the intake air stream of a CIE. This fuel burns and becomes a partial contributor to the power-producing fuel. While alcohol and gasoline may be used, gaseous fumigation seems to exhibit the best overall power yields, performance, and emissions benefits. Rudolph Diesel’s 1901 patent mentions the diesel fumigation process. Not until the 1940s were there any commercial
fumigation applications. Fumigation with propane was studied as a means to reduce injector coking (Peterson et al., 1987). Fumigation is a process of introducing alcohol into a diesel engine (up to 50%) by means of a carburetor in the inlet manifold. At the same time, the diesel pump operates at a reduced flow. In this process, D2 fuel is used for generating a pilot flame, and alcohol is used as a fumigated fuel (Demirbas, 2005). Alcohol is used as a fumigated fuel. At low loads, the quantity of alcohol must be reduced to prevent misfire. On the other hand, at high loads, the quantity of alcohol must also be reduced to prevent preignition. (Engine Performance Tests)

In dual injection systems, a small amount of diesel is injected as a pilot fuel for the ignition source. A large amount of alcohol is injected as the main fuel. It must be noted that the pilot fuel must be injected prior to injection of alcohol. Some ideal results can be achieved when this method is used. The thermal efficiency is better. At the same time, NOx emissions are lower. Moreover, CO emissions and HC emissions are the same. However, the system requires two fuel pumps, thus resulting in a high cost. Meanwhile, alcohol requires additives for lubricity (Demirbas, 2006b).

A visual inspection of the injector types would indicate no difference between the biodiesels when tested on D2 fuel. The overall injector coking is very low. Linear regression can be used to compare injector coking, viscosity, percent of biodiesel, total glycerol, and combustion heat data with the other physical properties such as flash point and cetane number (Demirbas, 2005).

Antioxidants tert-butylhydroquinone (TBHQ) and α–tocopherol showed beneficial effects on retarding the oxidative degradation of methyl soyate (biodiesel)
under the conditions of this study. Results indicated that v and AV have the best potential as parameters for timely and easy monitoring of biodiesel fuel quality during storage (Dunn, 2002). TBHQ is the most effective antioxidant for highly unsaturated vegetable oils and many animal fats. (Engine Performance Tests)

When a diesel engine is operated with biodiesel, exhaust emissions decrease; approximately 20% in CO, 30% in HC, 40% in particulate matter (PM), and 50% in soot emission, compared to the diesel fuel. In contrast to these decreases, its NOx emission increases about 10–15%. However, the high NOx problem can be overcome by retarding the injection timing. (M. Canakci, 2008)

Used frying oils, soap stocks, yellow and brown greases are potential feedstocks for biodiesel production to lower the cost of biodiesel. Used frying oils and fats are currently collected from large food processing and service facilities where they are rendered and used primarily in animal food. Soap stock is the by-product of edible oil refining that is substantially less expensive than edible-grade refined oils. Its market value is about one-fifth of the crude vegetable oil prices. Rendered animal fats and used frying oils with free fatty acids (FFA) level of less than 15% are known as yellow grease. If the FFA level exceeds 15%, it is named as brown grease. These feedstocks are attractive with their low cost. However, their transesterification reactions are much more difficult compared to those of food-grade high quality oils. They generally contain large amounts of FFA and water that cannot be converted to biodiesel using an alkaline catalyst. Waste greases typically contain FFA in the range from 10 to 25%. (M. Canakci, 2008)
When a fuel with lower density and viscosity is injected, improved atomization and better mixture formation can be attained. Like viscosity, the heating content of a fuel is a function of its density. Fuel density also affects the exhaust emissions. The density can be correlated with particulate matter (PM) and NOx emission. The fuel which has high density generally causes an increase in PM and NOx emission in diesel engines. The chain length and saturation level of the fuel raise the density. Thus, biodiesels produced from feedstocks such as fats or greases have more saturated fatty acids than the biodiesels produced from vegetable oils. But, this rise in the density is not a problem in terms of the required standard value. (M. Canakci, 2008)

The cetane number is related to the ignition delay time that is the time between the start of injection and start of combustion. As the cetane number increases, the ignition delay decreases and the main combustion phase (diffusion controlled combustion) increases. Long ignition delay is not acceptable since it causes diesel knock. Cetane number can also influence the cold engine starting and subsequent white smoke and noise emissions. (M. Canakci, 2008)

If the cetane number of a diesel fuel is too high, this fuel will ignite in a short distance to the injector and cause excessive heating of the injector. As the result of the intense heating, cooked fuel particles inside the injector may plug the injector nozzle. Because of this, cetane number of a diesel fuel should not be higher than 65. (M. Canakci, 2008)

To observe the effect of cetane number on a direct injection diesel engine performance, Icingur and Altiparmak conducted engine tests. For this purpose, the fuels
with 46, 51, 54.5 and 61.5 cetane number were tested at 150-bar injection pressure and full load conditions. The results showed that the engine torque and power output increased by 5 and 4%, when the cetane number was increased from 46 to 54.5, respectively. Nevertheless, when increasing the cetane number above 54.5, no significant increases were observed in the engine performance. (M. Canakci, 2008)

The CN has an inverse relationship to the ID. Higher CN has been correlated with reduced NOx emissions, although this may not always hold for all types of engine technologies. (N. Ladommatos, 1996)

Incomplete combustion is most likely to occur at low air-to-fuel ratios in the engine. These conditions are common during vehicle starting when air supply is restricted, when cars are not tuned properly, and at altitudes where “thin” air effectively reduces the amount of oxygen available for combustion. Two thirds of CO emissions come from transportation sources, with the largest contribution coming from highway motor vehicles. In urban areas, the motor vehicle contribution to CO pollution can exceed 90%. (Engine Performance Tests)

Nitrogen oxides (NOx) are gases formed in great part from atmospheric nitrogen and oxygen when combustion takes place under conditions of high temperature and high pressure; they are considered major air pollutants and precursors of ozone. (Engine Performance Tests)

Hydrocarbon (HC) emissions result when fuel molecules in the engine burn only partially. HCs react in the presence of nitrogen oxides and sunlight to form ground-level ozone, a major component of smog. (Engine Performance Tests)
Sulfur oxides (SOx) are pungent, colorless gases formed primarily by the combustion of sulfur-containing fossil fuels, especially coal and oil. (Engine Performance Tests)

The standard measure of the energy content of a fuel is its heating value (HV), sometimes called the calorific value or heat of combustion. In fact, there are multiple values for the HV, depending on whether it measures the enthalpy of combustion (ΔH) or the internal energy of combustion (ΔU), and whether for a fuel containing hydrogen product water is accounted for in the vapor phase or the condensed (liquid) phase. With water in the vapor phase, the lower heating value (LHV) at constant pressure measures the enthalpy change due to combustion (Jenkins et al., 1998). The HV is obtained by the complete combustion of a unit quantity of solid fuel in an oxygen-bomb calorimeter under carefully defined conditions. The gross heat of combustion or higher heating value (GHC or HHV) is obtained by the oxygen-bomb calorimeter method as the latent heat of moisture in the combustion products is recovered. (Engine Performance Tests)

Carbon deposits inside the engine were normal, with the exception of intake valve deposits. The results showed the transesterification treatment decreased the injector coking to a level significantly lower than that observed with D2 fuel (Demirbas, 2003).

The chain length of the compounds appears to have little effect on NOx and PM exhaust emissions, while the influence is greater on HC and CO. Non-saturation in the fatty compounds causes an increase in NOx exhaust emissions (Knothe et al., 2006)

Ignition quality of a fuel can be deduced though its cetane number. A fuel with good ignition quality has a high cetane number, where ignition delay period between the
start of fuel injection and the onset of auto ignition is short. A short ignition delay period lowers the peak combustion temperature which suppresses NOx formation. Cetane number of biodiesel varies with the feedstock used, but is generally in the higher end of the typical No. 2 diesel fuel range. The value of cetane number is found to generally increase with increasing carbon chain length. This is due to the higher concentration of hydroperoxyalhyl radicals, which is the principal source of chain-carrying OH radicals pertinent during fuel injection phase. (Jo-Han Ng, 2010)

Cetane number decrease with an increase in the number of double bonds, or when double bonds and carbonyl group move towards the center of the chain. (Graboski and McCormick 1998) Heat of combustion is found to increase with carbon chain length. (Knothe 2005)

Quenching of free radicals during combustion through the use of antioxidants could potentially control NOx formation, where the antioxidants donate hydrogen atoms to interfere with radical propagation reactions to force radical termination that inhibits oxidation. (Jo-Han Ng, 2010) “The start of combustion as indicated by the burning of 10% fuel mass” (Jo-Han Ng, 2010)

The start of combustion is taken as the angle value at which rate of apparent heat release changes from negative to positive. The start of injection is defined as crank angle at which the needle of nozzle lifts by 5%. (Ignition Delay in a Diesel Engine)

The combustion of biodiesel alone provides over a 90% reduction in total unburned hydrocarbons and 75 to 90% reduction in polycyclic aromatic hydrocarbons. Biodiesel also provides significant reductions in particulates and carbon monoxides than
petroleum diesel fuel. Biodiesel provides a slight increase or decrease in nitrogen oxides depending on the engine family and testing procedures. (Gerpen, Fuel Properties of Biodiesel, 2007)

Methanol has a higher octane rating than gasoline. Methanol has a high vaporization heat that results in lower peak flame temperatures than gasoline and lower nitrogen oxide emissions. Combustion of methanol with higher air-to-fuel equivalence ratio results in generally lower overall emissions and higher energy efficiency. Methanol is highly flammable and colorless when ignited and mix in all proportions with water due to the polar nature of the OH group. The high latent vaporization heat of alcohols cools the air entering the combustion chamber of the engine, thereby increasing the air density and mass flow, which leads to increased volumetric efficiency and reduced compression temperatures. The heat of combustion of alcohol is approximately half that of iso-octane. Methanol is not miscible with hydrocarbons and separation ensues readily in the presence of small quantities of water, particularly with a reduction in temperature. Anhydrous ethanol is completely miscible in all proportions with gasoline, although separation is effected by addition of water or by cooling. If water is already present, ethanol has a higher water tolerance than methanol and can be improved by the addition of higher alcohols, such as butanol. Benzene or acetone can also be used. The wear problem is believed to be caused by formic acid attack when methanol is used or acetic acid attack when ethanol is used. (Gerpen, Fuel Properties of Biodiesel, 2007)

Engine tests demonstrated that methyl esters produced slightly higher power and torque than ethyl esters. (Encinar et al., 2002)
Ethyl esters have significantly lower smoke opacity, lower exhaust temperatures, and lower point, but tend to have more injector coking than methyl esters. (Gerpen, Fuel Properties of Biodiesel, 2007)

Previous experiments using a 10% vol. biodiesel blend (palm oil feedstock) on common-rail engine were performed. The experiments included measurement of the in-cylinder pressure, regulated pollutants emissions and fuel consumption. The palm-oil biodiesel resulted in both higher and lower smoke and NO$_x$ emissions over the engine map. This was attributed to the effects of both the chemistry and the physical properties of the biodiesel. An analysis of experimental data of neat biodiesel to diagnose how various key performance parameters are affected by the use of 100% palm olein biodiesel was done by Brandon et al, (2009). The study identifies that fuel-air ratio and inlet mixture density tend to increase with biodiesel while volumetric efficiency tends to decrease with biodiesel. Exhaust nitric oxide emissions tend to increase and smoke concentrations tend to decrease with the use of biodiesel.

Manbae et al, (2008), investigated the effects of soybean and coconut-derived biodiesel fuels on combustion characteristics in a direct injection, common rail diesel engine. In conventional diesel combustion mode, particulate matter (PM) and nitrogen oxides (NOx) emissions were similar for all fuels studied except soybean B20. Soybean B20 produced the lowest PM but the highest NOx emissions.

Mueller et al, conducted experiments in a single-cylinder version of a heavy-duty diesel engine with extensive optical access to the combustion chamber. He operated an engine using two biodiesel fuels and two hydrocarbon reference fuels, over a wide range
of loads. Results suggest that the biodiesel NOx increase is not quantitatively determined by a change in a single fuel property, but rather is the result of a number of coupled mechanisms.

Zhang, (2008), studied combustion and emission characteristics of diesel and biodiesel blends (soybean methyl ester) in a single-cylinder Direct Injection (DI) engine. The results showed that NOx emission and fuel consumption increased with increasing biodiesel percentage. Reduction of smoke opacity was significant at higher loads with a higher biodiesel ratio. Compared with the baseline diesel fuel, B20 (20% biodiesel) has a slight increase of NOx emission and similar fuel consumption. Smoke emission of B20 is close to that of diesel fuel.

Patterson et al, (2006), used methyl esters derived from vegetable oils by transesterification as an alternative fuel in compression ignition engines. In this study, three different vegetable oils (rape, soy and waste oil) were used to produce biodiesel fuels that were then tested in direct injection engine. Engine performance and emissions for all of the 5% biodiesel blends were indistinguishable from mineral diesel. However, at higher blends, the rape fuel exhibited better emission and performance characteristics than either the soy or waste fuels. Furthermore, whilst emissions trends varied for each blend and fuel, emissions of smoke were significantly reduced at all speed and load conditions, and NOx was reduced by up to 50% at low loads. It will also be shown that while engine performance was not significantly deteriorated by biodiesel, there was evidence of increased ignition delay with higher blends, and a possible two-stage ignition process where mineral diesel ignited earlier than the biodiesel.
Kong et al (2008), measured particulate matters, nitrogen oxides, and carbon monoxides emissions using diesel/biodiesel blends. Tests were performed using the regular diesel fuel and biodiesel blends (B10, B20, B100). Test results showed that particulate matters and carbon monoxides decreased significantly as biodiesel content increases, whereas nitrogen oxides increased.

Grimaldi et al (2006), worked to evaluate the potentialities of bioderived diesel fuels, the effect of fueling an automotive diesel engine with biodiesel and fossil/biodiesel blend on its emission and combustion characteristics. The fuels tested were, a 50% biodiesel blend in the reference diesel, and a 100% biodiesel, obtained by mixing rape seed methyl ester (RME) and recycled cooking oil (CME). Experimental evidences showed appreciably lower CO and HC specific emissions and a substantial increase in NOx levels. A significant reduction of smoke emissions was also obtained.

Beatrice et al (2009) made an experimental evaluation of the impact of the diesel/biodiesel blends and presented it in terms of engine performances and pollutant emission analysis. In-cylinder combustion evolution and injection law characterization were carried out on a single cylinder engine, on an optical single cylinder engine and on an injection test rig. Increasing the biodiesel percentage a reduction mainly in terms of smoke emission was observed. The engines performance, as well as the pollutant emissions, was not substantially changed. Eckerle et al (2008), studied the effects of methyl ester biodiesel fuel blends on NOx emissions experimentally and analytically. A precisely controlled single-cylinder diesel engine experiment was conducted to determine the impact of a 20% blend of soy methyl ester biodiesel (B20) on NOx emissions. In
addition, the impact on the engine control system of the lower specific energy content of biodiesel was determined. Because the magnitude and even direction of NO$_x$ effect changes with engine load, the NO$_x$ effect associated with burning biodiesel blends over a duty cycle depends on the duty cycle average power and fuel cetane number. In his work, the difference in NO$_x$ emissions between a B20 and its base diesel fuel was relatively small.

The fuel properties, the diesel combustion and the exhaust emissions of palm kernel oil methyl ester (PKME) and a blend of 20% PKME with gas oil (PK-B20) were investigated by Myo (2007). In this study, the fuel properties were measured by laboratory analyses and the engine experiments were carried out by using a single-cylinder direct injection diesel engine. To make comparison between biodiesels and conventional diesel fuel, palm oil methyl ester (PME), coconut oil methyl ester (CME), and the gas oil were also used as test fuels. From the fuel property analyses and the engine experimental results; the pour point of PKME was the same as that of CME and the pour point of PK-B20, the brake thermal efficiency of PKME was the same as the other test fuels, the ignition ability of PKME was better than that of the gas oil and the exhaust emissions (CO, HC, NOx and smoke) from PKME were almost the same as those of CME and lower than those of the gas oil.

Bennadji et al. (2009) studied the autoignition delay times of methyl crotonate, methyl acrylate, ethyl butanoate, ethyl crotonate, and ethyl acrylate in shock tube experiments. A series of mixtures diluted with argon, of varying fuel/oxygen equivalence were measured behind reflected shock waves at temperatures of 1280-1930 K, and
pressures 7-9.65 atm, and found that the ignition delay time decreases as temperature rises.

Feng et al. (2010) studied in a stagnation-flow reactor configuration, which allows for the systematic evaluation of fundamental combustion and emission characteristics, the oxidation characteristics of biodiesel fuels of pure fatty acid methyl-esters (FAME,) that can serve as surrogate compounds for real biodiesels. The focus was on the pollutant emission characteristics of two low carbon fuels: C4 FAMEs: ethyl-butanoate and methyl-crotonate, whose behavior is compared with that of n-butane and n-pentane. The effects of chain length and degree of saturation on the fundamental flame properties of these fuels were evaluated. NOx concentration profiles were measured in stagnation flow flames by sampling using a quartz micro-probe followed by chemiluminescence analysis.

Knothe et al. (1998) injected into a constant-volume combustion apparatus, fatty acids of C18 chain length as well as their methyl, ethyl, n-propyl, and n-butyl esters that were suitable for collecting material from the fuel spray prior to the onset of ignition. The collected material from this precombustion phase of the injection event was analyzed by gas chromatography–mass spectrometry (GEMS). Compounds identified as forming during the precombustion phase were straight-chain and branched alkanes, alkenes, and cyclic hydrocarbons, as well as aldehydes, ketones, esters, substituted benzenes. Some of the compounds formed during precombustion have low cetane numbers (CN) more prominently for more unsaturated fatty compounds.

McCormick et al. (1997) investigated 1% oxygen in diesel using a 6V-92TA DDEC II engine. Oxygen was added as a C8 (n-octanol), C12 (decanoic acid), and C17
(methyl soyester) [21]. Relative to the base diesel, the NOx changes were 1-2.29%. This study also examined the effect of n-octanol and methyl soyester at 2% oxygen on NOx emissions. Octanol reduced NOx by 2.9% while methyl soyester increased NOx by 2.53%. The data suggest that lower molecular weight or lower boiling point oxygenates might not affect NOx as greatly as methyl soyester.

Williams et al. (2010) investigated which biodiesel fuel properties impact reactivity. Three fuel properties in this study included fuel oxygen content and functionality, fuel aromatic content, and the presence of alkali metals. Results showed no dependence on the aromatic content or the presence of alkali metals in the fuel. The presence and form of fuel oxygen proved to be the dominant contributor to faster DPF regeneration times and soot reactivity. The form of the oxygen functional group proved to play a role in DPF performance, and a long-chain alcohol (a carbon bonded to a single oxygen atom) provided a more effective form of oxygen than the methyl-esters of biodiesel (a carbon bonded to two oxygen atoms) for improving soot reactivity.

Ban-Weiss et al. (2007) evaluate proposed theories for slight NOx increase, including based on biodiesel’s cetane number, which leads to differing amounts of charge preheating, and theories based on the fuel’s bulk modulus, which affects injection timing. They propose an additional theory for the slight NOx increase of biodiesel. Biodiesel typically contains more double bonded molecules than petroleum derived diesel and these double bonded molecules have a slightly higher adiabatic flame temperature, which leads to the increase in NOx production for biodiesel. The theory was verified using numerical simulations to show a NOx increase, due to the double bonded molecules, that is
consistent with observation and the numerical simulations show that NOx is predominantly due to the Zeldovich mechanism.

Sun et al. (2010) investigated the differences in properties between biodiesel and petroleum diesel fuels that create several changes to system and combustion behaviors of diesel engines. They found that combined, these effects lead to several complex and interacting mechanisms that make it difficult to fundamentally identify how biodiesel affects NOx emissions. Instead, several parameters seem to influence on the observed differences in NOx emissions with biodiesel, thus introducing several possibilities for inconsistency in the trends. These parameters are injection timing, adiabatic flame temperature, radiation heat transfer, and ignition delay.

Detailed analysis shows that ignition delay and exhaust emissions are affected by the proportion of biodiesel. Biodiesel’s higher surface tension may contribute to an advance in injection timing; its influence on ignition delay is complex due to competing interactions with atomization, droplet size, penetration, and evaporation. Biodiesel’s lower heat capacity may allow its temperature to rise at a faster rate once injected, and droplets evaporate sooner than petroleum diesel, contributing to shorter ignition delay. In terms of chemical properties, the literature tends to identify the increased double-bonding of biodiesel as contributing to shorter ignition delays. Thermal cracking of double-bonds associated with unsaturated fatty acids during injection results in breakdown of high molecular weight species to lower molecular weight species on the periphery of the fuel spray, allowing their mixing and eventual ignition with air. These mechanisms are believed to allow shorter ignition delay compared to more saturated fuel structures.
However, Ryan et al. note that increased viscosity with biodiesel decreases atomization, mixing rate, and cone angle, which should contribute to increased ignition delay. They conclude that the balance between chemical and physical mechanisms results in a net decrease in ignition delay.

This study aimed to determine the appropriate engine decision making for the air/fuel ratio (AFR), exhaust gas recirculation (EGR) fraction, injection (rail) pressure, and start of main fuel injection (SOI) in a modern common rail diesel engine using variable geometry turbo-charging and operating with varying blend ratios of diesel and soy-based biodiesel fuel mixtures to minimize brake-specific fuel consumption (BSFC) and adhere to strict combustion noise, NOx and particulate matter (PM) emission constraints. When operating with the stock engine decision making, biodiesel blend combustion resulted in increases in NOx of up to 39% and fuel consumption increases up to 20% higher than the nominal diesel levels but also had substantial reductions in PM. Through modulation of the AFR, EGR fraction, rail pressure, and SOI at several operating points, it was demonstrated that the optimal engine decision-making for biodiesel shifted to lower AFRs and higher EGR fractions in order to reduce NOx, and shifted to more advanced timings in order to mitigate the observed increases in fuel consumption at the nominal settings. The optimal parameter combinations for B5, B20 and B100 still maintained substantial PM reductions but resulted in NOx and noise levels below nominal diesel levels. However, these parameter combinations had little impact on reducing the biodiesel fuel consumption penalty but did improve the thermal efficiency of biodiesel blend combustion. The engine used at Purdue University’s Herrick
Laboratories for these studies was a 2007 Cummins ISB 6.7 liter inline-six cylinder turbo-diesel engine fitted with common rail fuel injection, externally-cooled EGR, and VGT.

Optimal engine settings including lower AFR, higher EGR fraction, and earlier start of main injection, the biodiesel-NOx effect can be mitigated with blends of soy-based biodiesel in a modern diesel engine while simultaneously keeping BSPM and noise at or below the level of diesel. However, these optimal settings will have limited net effect on counter-acting the lower energy density effects of biodiesel. (David Snyder, 2010)

Recent advancements have demonstrated new combustion modes that exhibit low nitric oxide emissions and high thermal efficiencies. These new combustion modes involve various combinations of stratification, lean mixtures, high levels of EGR, multiple injections, variable valve timings, two fuels, and other such features. Although the exact combination of these features that provides the best design is not yet clear, the results (low emissions with high efficiencies) are of major interest. The current work is directed at determining some of the fundamental thermodynamic reasons for the relatively high efficiencies and to quantify these factors. Both the first and second laws are used in this assessment. An automotive engine (5.7 liter) which included some of the features mentioned above (e.g., high compression ratios, lean mixtures, and high EGR) was evaluated using a thermodynamic cycle simulation. These features were examined for two operating conditions: a moderate load, moderate speed condition (“A”), and a lower load, lower speed condition (“B”). By the use of lean operation, high EGR levels,
high compression ratio and other features, the net indicated thermal efficiency increased from 35.6% to 48.2% (condition “A”), and from 30.3% to 44.6% (condition “B”). These increases are explained in a step-by-step fashion. One of the major reasons for these improvements was the lower heat losses associated with the advanced conditions.

The final case for condition “A” (bmep = 900 kPa) resulted in a net indicated efficiency of 48.2% and a brake efficiency of 41.6% with negligible nitric oxide emissions. To obtain the bmep of 900 kPa, the inlet pressure needed to be about 227 kPa. This will require a turbocharger or supercharger. Since the exhaust gas energy is significantly decreased (exhaust temperature was 642 K), the use of a turbocharger may be problematic. Increasing the compression ratio from 8.0 to 20.0 provided one of the more effective ways to increase the efficiencies for both conditions. Decreasing the equivalence ratio from 1.0 to 0.7, and increasing the exhaust gas recirculation to 50% provided significant efficiency gains largely due to the significant decrease of the relative heat transfer and the increase of the ratio of specific heats during the expansion stroke. Decreasing the burn duration from 60 °CA to 30 °CA increased the net indicated efficiency only a modest amount. At least part of the reason for the modest increase was due to the use of MBT timing. Increasing the cylinder wall temperature from 450 K to 550 K increased the efficiencies only very slightly. Some of the gains suggested by the increases of the net indicated thermal efficiency are somewhat mitigated in terms of the brake efficiencies. This is due to the increased cylinder gas pressures (that are necessary to obtain the same load) which increase the mechanical friction component. (Caton, 2010)
The experimental results of well known formulae for calculating mass of soot using FSN and elemental carbon mass using thermal optical analysis (TOA) over a range of operating conditions and fuels from a four cylinder direct injection passenger car diesel engine. The data show that the mass of soot emitted by the engine can be accurately predicted with the smoke meter method utilizing a 3000 ml sample volume over a range of FSN from 0.02 to 1.5. Soot mass exhaust concentration calculated from FSN using the best of the literature expressions and that from the TOA taken over all conditions correlated linearly with a slope of 0.99 and R2 value of 0.94. A primary implication of the work is that the level of confidence in reporting soot mass based on FSN for low soot formation regimes like LTC is improved for both petroleum diesel and biodiesel fuels (William F. Northrop, 2010).

Soot mass exhaust concentration calculated from FSN using the correlation developed by Christian et al. and that measured from the TOA taken over all conditions correlated linearly with a slope of 0.99 and R2 value of 0.94. Based on the findings, confidence in the use of such correlations is improved in estimating soot mass for engine conditions where FSN is lower than that for which they were originally developed and for oxygenated fuels that result in higher semi-volatile fraction on the particulate. Further, it can be concluded that development of a new correlation for soot mass emissions is not necessary for low FSN achieved in LTC modes of operation or for when biodiesel blends are used (William F. Northrop, 2010).

The following are results discussed by S. L. Kokjohn on combustion characteristics during conventional and low temperature diesel combustion. The results
show that even in the limit of mixing controlled combustion, the flame structure is captured extremely well without considering sub-grid scale turbulence-chemistry interactions. The combustion process is dominated by volumetric heat release in a thin zone around the periphery of the jet. The rate of combustion is controlled by transport of reactive mixture to the reaction zone and the dominant mixing processes are well described by the large scale mixing and diffusion. As the ignition delay is increased past the end of injection (i.e., positive ignition dwell), both the simulations and optical diagnostics show that the reaction zone spans the entire jet cross-section. In this combustion mode the combustion rate is no longer limited by transport to the reaction zone, but rather by kinetic timescales. Although comparisons of results with and without consideration of flame propagation show very similar flame structures and combustion characteristics, the addition of the flame propagation model reveals details of the edge or triple-flame structure in the region surrounding the diffusion flame at the lift off location. These details are not captured by the purely kinetics based combustion model, but are well represented by the present multi-mode model. Comparisons of early stage combustion images showed that even for a diffusion flame, pre-combustion mixing occurs. The level of this pre-combustion mixing determines the flame lift off length and thickness of the diffusion flame. In the limit of mixing controlled combustion (i.e., HTC-short ID), the reaction rate was controlled by the large scale transport of reactive mixture to the reaction zone. This gave the appearance of a thin diffusion lame on the outer edge of the spray plume. As the pre-combustion mixing time increased, it was found that the diffusion flame became thicker. Once the ignition delay was increased past the end of
injection, a diffusion flame was no longer observed and reaction was seen to occur completely across the jet cross section. In the limit of premixed combustion, it was found that the injection generated turbulence was dissipated significantly prior to auto-ignition; thus, the rate of energy release is dominated by chemistry effects, rather than turbulent transport. It was found that the results were very similar with and without use of the flame propagation model. However, the simulations using the flame propagation model revealed details of the edge or triple-flame structure in the region surrounding the diffusion flame at the lift off location. These details were not captured by the purely kinetics based combustion model. The major conclusion of this study is that flame structure is well predicted over the entire range from non-premixed to premixed combustion without the need to consider sub-grid scale turbulence chemistry interactions. (S. L. Kokjohn, 2010)

An LTC load management strategy to improve the energy efficiency of diesel LTC has been proposed that could enable LTC operation up to 10 bar IMEP through testing at 1500 and 1800 RPM on a modern high-compression ratio diesel engine. The strategy encompasses three LTC fuelling strategies, coupled with strict control on the EGR and combustion phasing. The single-shot LTC was enabled with heavy EGR to realize ultra low NOx and soot emissions at low loads (3~5 bar) and with a low energy-efficiency penalty. The single-shot LTC at moderate engine loads (up to 8 bar IMEP) incurred a very high CO and HC penalty and the ultra low soot levels were difficulty to attain. At higher engine speeds, the HC and CO penalty tends to rise rapidly and therefore, the single-shot LTC is more suited to low-speed operation. The multi-shot
LTC is largely applicable to mid-load engine operating conditions and was realized up to 7.5 bar IMEP with ultra low NOx and soot emissions with a low HC penalty. The load range of the multi-shot LTC was primarily limited by the high compression ratio that resulted in very high peak cylinder pressures, exceeding 160 bar and also very high maximum rate of pressure rise (>20 bar). At higher engine speed, the multi-shot strategy was demonstrated to achieve ultra low NOx and soot, with a moderate CO and HC penalty. The splitting of the heat release (split-injection LTC) helped to reduce the peak cylinder pressure and the maximum rate of pressure rise associated with the multi-shot LTC. The containment of the pressure levels enabled the load to be increased up to 9.7 bar IMEP. Ultra low soot is not attainable at mid-high loads with split-injection LTC because of the conventional burn of the near-TDC injection. The smoke readings were >2 FSN. An alternate DPF-tolerant smoke limit of 2.5 FSN was therefore used as the acceptable criterion. (Usman Asad, 2010)

The effect of 30% soybean oil biodiesel blend on the injection mass, exhaust emissions, engine power under part and full load operating conditions were investigated using a common-rail 4-cylinder diesel engine satisfying EURO- exhaust emission legislations. On using B30 instead of diesel, injection mass change was less than 1.7% at injection pressure of 60 and 120 MPa. Therefore it is evident that the injection mass change on using B30 is insignificant. At part-load operating conditions, NO\textsubscript{2} emission of B30 increased by 18% and the smoke number reduced by 55% under the same EMS configuration. At part and full load operating conditions, thermal efficiency did not deteriorate when B30 was used. However, power reduction of 2.1 ~ 3.8 % was observed.
at full load operating conditions using B30 without change of EMS modification due to the lower calorific heating value of B30 than diesel. A meaningful change was observed in O₂ concentration of exhaust gas when B30 was used, and the lower stoichiometric air-fuel ratio of B30, due to oxygen content in its molecular structure, was expected to increase O₂ concentration in the exhaust. B30 led to reduced exhaust gas temperatures compared to diesel and it can potentially contribute to the durability of exhaust systems. However, the side effects of exhaust gas after-treatment system, such as, activation of DOC and soot regeneration in DPF, should be investigated. At full load operating conditions, with the same torque of diesel, B30 showed about 19% reduction in smoke. (Myung Yoon Kim, 2010)

A skeletal mechanism with 118 species and 837 reactions was developed from a detailed LLNL mechanism for a biodiesel surrogate mixture with equal mole fraction of methyl decanoate, methy-9-decenoate and n-heptane, through subsequent applications of a revised method for directed relation graph (DRG), isomer lumping, and DRG-aided sensitivity analysis (DRGASA). The reduction was performed within a parameter range of pressure from 1 to 100atm, equivalence ratio from 0.5 to 2, and temperature above 1000K for both auto-ignition and perfect stirred reactors. The detailed mechanism consists of 3329 species and 10806 reactions. With the reduction in mechanism size by almost a factor of 30, the skeletal mechanism was shown to still feature a good accuracy for temperature higher than 1000K, both in predicting the system parameters, such as ignition delay and extinction time, and detailed species profiles, compared with the detailed mechanism. Numerical simulations in jet stirred reactors were also performed
and compared with experimental measurements for rapeseed oil methyl ester. This skeletal mechanism can be used to model methyl esters from different feedstocks since it is a tri-component mixture. While the mechanism was suitable to simulate high temperature applications such as that involving flame stabilization, it may not be applicable to simulations involving low-temperature ignition, particularly those in the negative temperature coefficients (NTC) zone. Reduced mechanisms covering low temperature chemistry are expected to be substantially larger in size and will be studied in the future work. (Zhaoyu Luo1, 2010)

Testing of the biodiesels produced from natural sources (supplied by IGT) indicated that PM emissions were dependent on the oxygen content of the fuel only. All fuels reduced PM and increased NO\textsubscript{x} relative to certification diesel. The mostly highly unsaturated fuels (canola and soy) produced the highest NO\textsubscript{x} emissions. Btu based fuel economy was the same for all biodiesels and certification fuel.

For the fuels prepared from nearly pure esters, the exceptions were methyl palmitate, methyl laurate, ethyl stearate, and ethyl ester of hydrogenated soybean oil. High peroxide value (1800), acid number, and glycerine content had no effect on regulated pollutant emissions in this short term study. Density of cetane number (which were highly correlated with each other), PM reduction was proportional to oxygen content for biodiesels with a cetane number of greater than about 45 (density greater than0.89). Neat biodiesels with cetane numbers greater than about 60 may produce NO\textsubscript{x} emissions equal to or less than certification fuel. More saturated esters have higher cetane numbers and lower densities than less saturated esters. Thus, the lower the iodine
number, the lower the NO\textsubscript{x} emission. The density of shorter chain length saturated esters is greater than longer chain saturated esters and the NO\textsubscript{x} emission is also greater. For example, methyl laurate, with a cetane number of 61.2 and density of 0.873, and is NO\textsubscript{x} neutral compared to certification fuel.

Data on emissions based on the EPA heavy-duty transient cycle are necessary to demonstrate the possible sensitivity of engine emission to biodiesel ester composition. A series of fuels consisting of nearly pure fatty acid esters was prepared for understanding the impact of biodiesel composition on emissions. Methyl-tertiary-butyl ether (MTBE) has been shown success in reducing emissions from gasoline engines. In high polluting automobiles oxygenated gasoline can decrease CO up to 50%.

Most of these oxygenates were cetane neutral (cetane number similar to diesel) so that the fuel cetane number was considered to be constant. Based on heavy-duty transient testing, CO was generally reduced, and NO\textsubscript{x} showed an increase with all oxygenates studied. Ethylene glycol monobutyl ether acetate was selected for testing and results showed CO and PM reductions of approximately 18% and a NO\textsubscript{x} increase of 3%. The NO\textsubscript{x} increase for methyl soyester (C\textsubscript{17}) is in good agreement with the Ortech work.

Fuel density is known to effect emissions of NO\textsubscript{x} from diesel engines. From Signer and coworkers report a 3 to 4% increase in NO\textsubscript{x} for a 3.5% increase in fuel density using the EEC 13 mode test cycle. For biodiesel blends with diesel, the blend aromatic content is lower than that of the base diesel fuel (oxygenates contain no aromatics). This dilution of the aromatics should lower both PM and NO\textsubscript{x} emissions.
There is strong evidence that higher boiling oxygenates such as soy derived biodiesel can cause NO\textsubscript{x} emissions to increase. The methyl soy ester was proposed that glycerine will impact emissions both immediately due to its different chemical structure and long term due to injector fouling. The acid number specification is related to corrosion and small amounts of free fatty acids in esters should have no real impact on measured emissions during short term test campaigns. The stearate and hydrogenated soy fuels had high melting points and were extremely difficult to work with, making removal of free fatty acid from these fuels by neutralization not feasible.

The iodine number of the fuels ranged from 0.5 to 165. Iodine number is directly related to chemical structure as it measures the degree of chemical unsaturation of the ester fuels. The tendency to oxidize is highly correlated with the iodine number of the fuel. To determine if oxidation produced instantaneous emissions effects, two soy fuels were contacted with air and the peroxide numbers of the fuels were raised considerably.

The original plan was to produce very pure esters so that the hypothesis that the emissions of a biodiesel from a natural fat source could be quantitatively predicted by a linear combination of emissions from the individual fatty acids in the fat. Iodine number is an easily measured property that provides information on chemical composition. This property is measured by titrating the olefinic bonds in the fuel to establish the weight of iodine required to fully saturate the molecule. For certification fuel tests results, the raw emissions for the various biodiesels and their blends need to be corrected by only a small amount at most for PM and do not need to be corrected for NO\textsubscript{x}. 
Methyl stearate and the mixture of methyl linseed with methyl stearate could not be successfully run because of handling problems with the fuels. It was difficult to keep the fuels from solidifying in the fuel system due to the high pour point of methyl stearate. The methyl linseed and methyl stearate blend was successfully run. It gave a NOx emission which seemed to be less than a linear combination of the blending agents but a particulate emission more characteristic of the tri-unsaturate. Even though these fuels can produce PM emissions which are lower than certification fuel, they produce much higher PM than saturated, mono and di-unsaturated fuels.

The PM emission for methyl stearate was high compared to other saturated esters, and this was probably related to difficulties in running the fuel. It had a pour point above room temperature and was very difficult to keep the fuel liquid during testing.

While density was used as the correlation parameter this does not mean that varying energy density is the primary explanation for the NOx variation. Cetane number can be used to discuss emissions effects. In order to get the full PM benefit, the cetane number of the biodiesel needs to exceed about 45. The cetane requirement for low NOx emissions is stronger than the demand for low PM emissions. PM appears impacted at cetane number values only less than present in conventional diesel fuels today.

A detailed analysis of the data was performed in an effort to determine what fuel properties are correlated with the increase in NOx emissions observed for biodiesel. All fuels tested met the water and sediment specifications as well as the free and total glycerine specifications, but not the acid number specification. The results indicate that all biodiesel fuels lowered PM relative to certification diesel. PM reduction was
proportional to oxygen content for biodiesels with a cetane number of greater than about 45. NOx emissions varied significantly with fuel composition but were well correlated with biodiesel density (Graboski, 1999).

Not all fuels met the acid number specification, in particular fuels with high stearate content as these were not liquid at or near room temperature making acid removal difficult. PM emissions did not depend on molecular structure but were dependent on the oxygen content of the fuel only, when testing the biodiesel produced from natural sources. The most highly unsaturated fuels (canola, soy, and soap stock) produced the highest NOx emissions. Soy and soap stock biodiesels produced very similar emissions (Graboski, 1999).

All reduced PM relative to certification diesel but the PM reduction was not proportional to oxygen content in all cases. No consistent difference in emissions was observed between ethyl and methyl esters of the same feedstock. High peroxide value (1800), acid number, and glycerin content had no effect on regulated pollutant emissions in this short-term study. Aldehyde emissions from the various biodiesels are not significantly different from aldehyde emissions from certification diesel fuel (Graboski, 1999).

More saturated esters have higher cetane numbers and lower densities than less saturated esters. Thus, the lower the iodine number, the lower the NOx emissions. The important conclusion is that fuel chemistry is at the root the fuel properties that effect emissions, and in particular the increased NOx emissions observed for many biodiesel fuels. Insufficient physical property data are available to characterize the effect of
blending at this time, although provisionally for 25 blends a linear combination of NO\textsubscript{x} emissions seems appropriate (Graboski, 1999).

Oxygenated compounds used as diesel additives are structurally similar to diesel fuel but have one or more oxygen atoms bonded to the hydrocarbon chain. Three glycol ethers, an aromatic alcohol, an aliphatic alcohol, and polyether polyol were selected for evaluation. Based on heavy-duty transient testing, PM and CO was generally reduced, and NO\textsubscript{x} showed an increase with all oxygenates studied. For example, Signer and coworkers (1996) report a 3% to 4% increase in NO\textsubscript{x} for a 3.5% increase in fuel density using the EEC 13-mode test cycle (Graboski, 1999).

There is strong evidence that soy derived biodiesel can cause NO\textsubscript{x} emissions to increase. The objective of the current investigation is to determine the effect of biodiesel source material and ester molecular structure (number of double bonds and chain length) on PM, NO\textsubscript{x} and certain unregulated pollutants. The iodine number of the fuels ranged from 0.5 to 165. Iodine number is directly related to chemical structure as it measures the degree of chemical unsaturation of the ester fuels. The presence of peroxide was shown through samples that were prepared under argon and every precaution was taken to eliminate contact with air, analyses of the fuels (Graboski, 1999).

Biodiesel from a natural fat source could be quantitatively predicted by a linear combination of emissions from the individual fatty acids in the fat. In this program, problems occurred that were associated with water evident indicating that the hygroscopic character of these esters can create problems during storage and transport. A second important observation is that the fuel was difficult to maintain in a liquid state.
The vehicle would stall on the road. Finally, fuels with a significant number of linolenic acid esters run poorly. This is probably due to the very low cetane numbers of these fuels.

Formaldehyde or acetaldehyde would be one of the expected majorities of the aldehyde emissions that the esters were made with methanol or ethanol. Methyl esters of soy, canola, and edible tallow did not produce emissions of total aldehydes or specific aldehyde species that are significant different from emissions from certification diesel. This could be caused by a higher free glycerine or glyceride content for this fuel, however analyses for these species reported by IGT do not show a higher glyceride content for this fuel. To conclude, aldehyde emissions from various biodiesels are not significantly different than aldehyde emissions from certification diesel fuel.

All biodiesel fuels produced higher NO$_x$ than certification diesel and all lowered PM relative to certification diesel due to hydrogenated soybean oil. Examination of the series suggests that longer chain esters have lower NO$_x$ emissions. Other testing included the effect of oxidation on regulated emissions and from an emissions standpoint oxidation had no effect. Oxidation would be expected to raise the cetane number of the fuel slightly. Out of specification impacts, both fuels gave identical emissions indicating that acid number has no effect on regulated emissions in short term emissions tests. The effect of the high glycerine content on PM emissions was not significant.

The investigation is to determine the effect of biodiesel source material and ester molecular structure (number of double bonds and chain length) on pollutant emissions. The effect on unsaturation in the hydrocarbon chain shows the effect of number of double bonds on NO$_x$ and PM emissions from methyl and ethyl esters of nearly pure fatty acids.
The number of double bonds has no consistent effect on PM emissions. For fuels containing a mixture of molecules the iodine number is a measure of the degree of unsaturation or number of double bonds. The relationship between iodine number and emissions of NO\textsubscript{x} and PM with emissions values for several specific fuels noted for reference is shown in figure 17. There is a highly linear relationship between iodine number and NO\textsubscript{x} and the regression predicts that a biodiesel with an iodine number of 38 will be NO\textsubscript{x} neutral relative to certification diesel. PM emissions do not vary with iodine number. Iodine number is highly inversely correlated with cetane number (high iodine number correlates with low cetane number). Thus, excessive ignition delay and poor combustion performance may also be proposed as a cause of the high NO\textsubscript{x}. Density and isentropic bulk modulus are also affected by number of double bonds and might also be the cause. The effect of hydrocarbon chain length results in decreasing fatty acid chain length or molecular weight will lower boiling point and viscosity, and affect other fuel properties. One direct comparison of the impact of chain length on emissions was performed in this study. We conclude that shorter chain esters produce higher NO\textsubscript{x} emissions. Therefore shortening of the hydrocarbon chain may be a route to NO\textsubscript{x} neutral fuels with improved properties. Chain length has no significant impact on PM emissions for this small dataset. As for number of double bonds, chain length impacts a number of fuel properties including cetane number, density, boiling point to name a few. If the cetane number is too low, the ignition will not occur at the time of injection and emissions and performance may deteriorate. Iodine number is not a good candidate as a
correlating parameter because saturated molecules of different chain lengths all exhibit an iodine number of zero. (Graboski 2003)

The purpose of this report was the study to compare biodiesel (transesterified soybean oil) and biodiesel/heavy alkylate blends with conventional petroleum diesel fuel when fueling a Cummins L10E. The National Biodiesel Board sponsored a research effort at BDM-Oklahoma (NIPER) to measure and compare: regulated EPA exhaust emissions, engine performance, and two NO\textsubscript{x} reducing strategies (timing retard and use of heavy alkylate). Heavy alkylate is a by-product of the alkylation process used in most modern refineries to create isoctane, a high octane, clean burning component for gasoline. The use of high boiling heavy alkylate with biodiesel/petroleum diesel blends could serve to relieve a potential problem for petroleum refineries.

A 1992 Cummins L10E engine was tested using an engine dynamometer under transient conditions by the Department of Mechanical and Aerospace Engineering at West Virginia University. The L10E was a four stroke, turbocharged, six cylinder engine of in-line configuration had a 10 liter displacement and was rated at 280 horsepower at 2000 rpm with peak torque of 900 lb-ft at 1200 rpm. The engine electronic control module (ECM) used when testing a standard injection timing was a standard control module used with the Cummins L10E engine. To determine EPA regulated exhaust emissions when the injection timing of the engine was retarded by 3˚, a different ECM was re-programmed by Cummins Engine Company.

For the experiment, three hot starts (6/7 weighting) and one cold start (at 1/7 weighting) were measured using the following fuels:
- DF = conventional low sulfur 2D petroleum diesel fuel
- B20 = a blend of 20% biodiesel with 80% DF
- B20A20 = a blend of 20% biodiesel and 20% heavy alkylate with 60% DF
- B30A15 = a blend of 30% biodiesel and 15% heavy alkylate with 55% DF

A B30 (a blend of 30% biodiesel with 70% DF) was also used to fuel the engine. All testing were ran using a transient cycle generated from the first torque map that was conducted using the base DF fuel on the first day of testing. The results of the testing were in agreement with biodiesel studies that had been conducted on other two and four stroke diesel engines.

As the biodiesel blend concentration increased, the total hydrocarbons (THC), carbon monoxide (CO) and particulate matter (PM) declined while the oxides of nitrogen (NO\textsubscript{x}) emissions increased. All EPA regulated exhaust emissions were reduced below that observed when fueling with baseline low sulfur diesel fuel as a result of timing changes and/or fueling with heavy alkylate blends. Maximum power and peak torque were slightly affected by fuel and timing changes. The maximum changes from baseline DF occurred with the B20A20 blend which caused a 2% loss in maximum power and torque. Each blend tested clearly reduced the THC emissions of the engine and the engine produced higher THC when fueled on heavy alkylate and biodiesel blends when compared to the biodiesel blends alone. There were no changes in THC emissions when retarding the injection timing.

When testing the engine, the trends observe concerning CO clearly indicated that as the level of biodiesel in the blend increases, CO levels emitted by the engine decline.
CO reductions ranged from approximately 16%-26% when fueling the L10E with biodiesel, biodiesel blends, and biodiesel heavy alkylate blends. Also as the concentration of biodiesel increased, the oxides of nitrogen emissions increased. The increase in the oxides of nitrogen emissions while fueling the L10E with a 20% biodiesel blend was 3.7%.

When testing the engine with B20, reduction in PM was noted and in addition, the 20% heavy alkylate to the B20 blend further reduced the particulate matter emissions. However, the addition of 15% heavy alkylate with the B30 blend increased the PM emissions for reasons unknown. The opacity (smoke) levels were quite low in all tests, including the DF fuel. (Marshall, 1995)

In the first part, sunflower oil and peanut oil were investigated, and in the second part, sunflower oil and soybean oil were investigated. The specific objectives of the project included determining: the effects of vegetable oil fuels on diesel engine thermal efficiency, the effects of vegetable oil fuel on gaseous and particle exhaust emissions, the feasibility of vegetable oils and vegetable oil/diesel fuel blends as diesel fuel extenders and for emergency use in the event of severe diesel fuel shortages. For part one, the general objective was to present to the technical community initial basic performance and emissions data obtained during the study. (Barsic, 1981)

The performance and emissions characteristics of a direct injected, naturally aspirated diesel engine operating on 100% sunflower oil, 100% peanut oil and 50% (by volume) mixtures of either sunflower oil or peanut oil with #2 diesel fuel were compared to baseline results using #2 diesel fuel. The same goes for sunflower oil and soybean oil
that was performed in the second part. Both blends for 50% tests were mixed in five
gallon lots, while the 100% vegetable oils were tested directly from the 55 gallon drums.
All the test fuel samples were considered crude vegetable oils, since no additives were
used, nor were the samples subjected to any further refining or degumming processes.
(Barsic, 1981)

A naturally aspirated (NA) engine was selected for evaluation of these vegetable
oil fuels for two reasons. First, an NA engine represents a large population of engines sol
in agricultural and construction equipment during the last 20 years. Secondly, an NA
engine is more sensitive to fuel quality due to the longer ignition delays and lower
performance injection equipment typical of this engine design. The test matrix consisted
of three speeds (1000 rpm, 1500 rpm, and 2200 rpm) and up to six values of power at
each speed for the five fuels. During performance and emissions data acquisition, general
test results and observations relevant to the vegetable oil fuels were also noted. An engine
cranking speed of 250 rpm, normal engine starts were obtained with each test fuel, but
before starting the test, the engine and fuel supply were allowed to stabilize at room
temperature of 25°C-30°C. All engine performance data was corrected to standard
atmospheric conditions as per SAE procedure J816b, Ref (8). (Barsic, 1981)

For the engine performance results, in the sunflower oil and peanut oil, and the
thermal efficiencies were slightly lower because of the mass flow increase up to 20%
while the power increase was no more than 6% and the same went for the sunflower oil
and soybean oil. Most of the engine performance comparisons for different fuels were
made at equal fuel energy delivery rates. Like fuel flow rate, indicated power, indicated
specific fuel consumption, thermal efficiency, and exhaust temperature. For exhaust emissions at maximum fuel delivery, the exhaust emissions were greatest at maximum fuel delivery where equivalence ratios are highest. For crude soybean oil and crude sunflower oil at maximum fuel delivery rate, the exhaust emissions expressed in grams/indicated kWh generally increased as more vegetable oil was substituted for diesel fuel. The NO\textsubscript{X} emissions in both parts were the least affected by the use of vegetable oil for diesel. (Barsic, 1981)

Both parts also had carbon monoxide emission rate for these vegetable oil fuels be about twice or greater than that of #2 diesel fuel. For exhaust emissions versus time, the crude vegetable oil fuels, the injection nozzle condition influenced exhaust emission and engine performance. (Barsic, 1981)

The purpose of the study was to provide a detailed comparison of performance and emissions data and to characterize the biological activity of the particulate soluble organic fraction for each fuel using the Ames Salmonlla typhimurim test. A single-cylinder, 0.36 L, D.I. diesel engine was operated on diesel fuel, sunflower seed oil, cottonseed oil, soybean oil, and peanut oil. When performing some prior work, no work dealing with aldehyde emissions or the health effects of particulate emissions could be found. They are suspected to be harmful to biological systems. (Jacobus, 1983)

All tests were run at a fixed compression ratio of 18:1 and a fixed injection timing of 27 degrees before top dead center. The vegetable oil was heated to 71 +or - 6°C to aid in the injection process. In fig. 6, there are typical pressure and needle lift traces comparing DF-2 to the vegetable oils. The difference was in the pressure traces were
most pronounce at 1/3 rack, with the vegetable oils burning later in the cycle. (Jacobus, 1983)

In conclusion, the following points were made: the gas phase emissions for the vegetable oils tested are slightly higher. However in the case of NO$_x$ at 2/3 and full rack, the vegetable oils show significantly higher values than for the baselines DF-2. (Jacobus, 1983)

Biodiesel has higher cetane number and consequently its ignition delay time is shorter compared to that of diesel fuel. The biodiesel fuels from feedstocks with long carbon chain and more saturated fatty acids such as fats or waste greases have higher cetane numbers than those of biodiesel produced from vegetable oils. However, if they are compared with each other, it is seen that the flash points of biodiesels from low-cost feedstocks are higher than those from vegetable oils since they have relatively more saturated fatty acid composition. With high cetane number and low volatility, the amount of fuel that burns in the premixed combustion decreases since the ignition delay ends sooner as well as the less fuel evaporates in this duration. Therefore, NOx emission decreases due to low combustion pressure and temperature (Canakci, 2008).

There are some advantages and disadvantages of biodiesel. The advantages of biodiesel compared to petro diesel include biodegradability, higher flash point, reduction of most regulated exhaust emissions, miscibility in all ratios with petro diesel, compatibility with the existing fuel distribution infrastructure, and inherent lubricity. The disadvantages of biodiesel are the technical problems that have persisted to the present are oxidative stability, poor low- temperature properties, and a slight increase in NO$_x$
exhaust emissions. By solving these problems simultaneously has proven difficult because the solution to one of the problems often aggravates another problem, which the behavior can be traced from the dependence of fuel properties on the fatty acid structure (Knothe, 2003).

It has been shown that the cetane number decreases with a decreasing chain length, an increased branching, and an increasing unsaturation in the fatty acid chain. The higher cetane number increased the ignition quality. Saturated esters possess poor cold-flow properties and unsaturated fatty esters have lower melting points, which are desirable for improved low-temperature properties but also have low cetane numbers and reduced oxidative stability, which is undesirable for a diesel fuel. There are several possible approaches to solving these problems (Knothe, 2003).

Biodiesel is a renewable, alternative diesel fuel of domestic origin derived from a variety of fats and oils by a transesterification reaction; thus, it consists of the alkyl esters, usually methyl esters, of the fatty acids of the parent oil or fat. An advantage of biodiesel is its potential to significantly reduce most regulated exhaust emissions, including particulate matter (PM), with the exception of nitrogen oxides (NOx). In this work, three fatty acid methyl esters, neat methyl laurate, neat methyl palmitate, and technical grade methyl oleate, were selected for exhaust emissions testing in a heavy-duty 2003 six-cylinder 14 L diesel engine with exhaust gas recirculation. These fuels were compared with neat dodecane and hexadecane as well as commercial samples of biodiesel and low-sulfur petro diesel as the base fuel, thus establishing for the first time a baseline of the exhaust emissions of neat hydrocarbon (alkane) fuels versus neat methyl
esters. All fuels were tested over the heavy-duty diesel transient cycle. PM emissions were significantly reduced with biodiesel and methyl oleate (about 77 and 73%, respectively), while reductions with methyl palmitate and methyl laurate were even greater (82-83%) compared to the petro diesel fuel. PM emissions with biodiesel only slightly exceeded the upcoming emissions standards, raising the possibility that biodiesel may meet these standards using only a diesel oxidation catalyst without employing a particulate trap. NOx emissions increased with biodiesel (about 12%) and technical grade methyl oleate (about 6%) but decreased (about 4-5%) with methyl palmitate and methyl laurate relative to those of the base fuel. PM emissions decreased (about 45-50%) with both dodecane and hexadecane. NOx emissions were reduced (around 15.5-16%) with dodecane and hexadecane compared to those of the petro diesel fuel. The methyl ester moiety influences exhaust emissions by reducing particulate matter considerably more than neat straight-chain hydrocarbons, which are enriched in “clean” petro diesel fuels, while NOx exhaust emissions, which showed little chain-length dependence, are less reduced. Thus, no future “clean” petro diesel fuel should be able to achieve the low PM exhaust emissions levels of biodiesel without additional additive treatments or support by engine technology. Unsaturated fatty esters show slightly increased NOx and PM emissions compared to their saturated counterparts. The soluble organic fraction of the PM emissions was higher for the ester fuels. Hydrocarbon (HC) and CO exhaust emissions were also determined. Although HC emissions were low, a strong effect of chain length was observed (Exhaust Emissions of Biodiesel, Petro diesel, Neat Methyl Esters, and Alkanes in a New Technology Engine, 2006).
The commercial biodiesel fuel, as well as the fatty compounds, significantly reduced PM exhaust emissions (75-83%) compared to the petrodiesel base fuel, while the two hydrocarbons found in petrodiesel achieved reductions of only 45-50%. However, NO\textsubscript{x} exhaust emissions were slightly increased with commercial biodiesel and technical grade methyl oleate, while methyl laurate and methyl palmitate as well as dodecane and hexadecane led to a slight decrease of NO\textsubscript{x} compared to the base fuel. The chain length of the compounds had little effect on NO\textsubscript{x} and PM exhaust emissions, while the influence was greater on HC and CO, the latter being reduced with decreasing chain length. Unsaturation in the fatty compounds causes an increase in NO\textsubscript{x} exhaust emissions. The present results differ from previous literature data showing the effect of newer engine technology on exhaust emissions. The low levels of PM observed with the ester fuels may influence emissions reduction technologies when using biodiesel (Exhaust Emissions of Biodiesel, Petro diesel, Neat Methyl Esters, and Alkanes in a New Technology Engine, 2006).
Chapter 3

Methodology

Introduction
This chapter describes the method of fuel synthesis, fuel property analysis, engine data collection, and testing parameters. The subproblems mentioned in chapter 1 are approached and solutions discussed. Different instruments used and their calibration are discussed, along with the data acquisition (DAQ) and testing method.

Overview
The method of synthesis of fuels used an alkali catalyst reaction, test fuels were then analyzed to determine viscosity, rate of vaporization, periods of thermal reactions, and energy content. Combustion and emissions analysis was conducted of using a single cylinder naturally aspirated four stroke CI engine made by Kubota with a separate three vortex combustion chamber. This engine is instrumented with many sensors, which are discussed herein, but the sensors of main concern are as follows: rotary encoder, piezoelectric high pressure sensor with amplifier, fuel line pressure sensor with amplifier, high speed oscilloscope, laminar air flow meter, NO\textsubscript{X} analyzer, and smoke meter.

Transesterification of Peanut FAME
Transesterification is the process in which triglycerides (bio-oil) are mixed with methanol and a catalyst (NaOH) to produce methyl esters (biodiesel). Glycerol is a byproduct of transesterification. Measure 500.0 grams of bio-oil into 1 L beaker and place on hot plate stirrer. (with stirrer). Mix Methanol and NaOH under the ventilation


hood. Proper safety attire should be worn while handling hazardous chemicals. Measure 150 mL of methyl alcohol and pour into 500 mL Erlenmeyer flask. (make sure to stopper the flask, methanol will pull water from the air which can dampen the reaction) Measure 5.0 grams of NaOH on digital scale using a hexagonal weighing dish. (cover NaOH immediately or pour into methanol, NaOH will pull water from the air which can dampen the reaction) 150 mL of methyl alcohol should be mixed with 5.0 grams of NaOH, until the NaOH is completely dissolved. Once NaOH is completely dissolved mix the Methanol-NaOH solution into the bio-oil. Set digital hot plate to maximum temperature while magnetic stirrer running on high (9) rpm. When the temperature reading on the thermocouple reaches 35 degrees C, reduce the hot plate temperature gauge to 300 degrees. When the reaction reaches 58 degrees C, turn off the hot plate and monitor the temperature of the reaction while continuing to stir. **(Remember to the temperature needs to stay between 60-65 degrees C) If the temperature begins to drop, turn on the hot plate and set the temperature to 150 degrees. If the temperature appears to be going over
65 degrees C, remove the reaction vessel from the hotplate stirrer until the temperature returns to the appropriate range. Continue to stir at high rpm while keeping heat between 60-65°C for the first 30 minutes. After the first 30 minutes, slow the rpm of the stirrer to 6 for 20 minutes. For the last 10 minutes, run at a low (3) rpm. After 1 hour pour the contents of the 1 L beaker into the separatory funnel. Place the funnel on a ring stand located under the vent hood. Close the vent hood door. A minimum of 8 hours is required for the transesterification process to be complete. The mass of biodiesel produced should equal the mass of bio-oil used (500 grams). Likewise, the amount of glycerol separated out should equal the amount of methanol used (150 mL). Once transesterification is complete, drain the glycerol from the funnel into a plastic jar and seal. The glycerol will be held for waste assessment research. The esterified crude bio-oil (biodiesel) then undergoes several wash cycles of warm water and light agitation. The wash removes residual NaOH, methanol and glycerin. Care must be taken not to aggravate the biodiesel. Washing must be done gently and carefully so as not to mix the fuel and water. If mixed, separation time is considerably longer. Proper safety attire should be worn while handling hazardous chemicals. Water from the laboratory faucet will reach the desired temperature for washing crude esterified bio-oils. Set the water temperature to approximately 36.7 C and add approximately 500 mL to a 1 L beaker. Gently pour the water into the separatory funnel with biodiesel. The water should be slowly poured down the inside wall of the funnel and not directly into the middle of the fuel. Secure the funnel top and gently turn the funnel end over end for 30 seconds. Drain
of the water and repeat the process 5 times or until the water is clear. Wash water should be drained into a jar and held for waste assessment research.

To remove moisture molecules trapped in the fuel from the esterified crude bio-oil, dry air is bubbled through the fluid using an aerator. Perform drying operations under a ventilation hood. Ensure the adjustable air valve is closed and connect the aerator to an air source. Open the air source valve first. Lower the aerator into the separatory funnel and slowly open the adjustable valve until air begins to bubble through the fluid. Adjust the valve so that air gently bubbles throughout the fuel. Dry for a minimum of three hours or until fuel appears clear. The resulting product should be clean, esterified crude bio-oil ready for testing. Drain any sediment into a jar and hold for waste assessment research.
Drain the remaining, clean, fuel through the in-line filter and into storage jars. Create a Biodiesel Identification Number and label all storage jars.

Once dried, the fuel must pass through an inline filter before it is safe to run through an engine. This process removes residual glycerol and any other foreign contaminants that may still be present in the fuel. Gather the following equipment:

- Rocker 300 vacuum pump
- 3 ft. length of ¼” clear polyurethane tubing
- 250 ml Büchner flask (Vacuum flask)
- Büchner Funnel
- Filter Paper

Attach one end of the polyurethane tubing to the ribbed nozzle on the vacuum pump and the other end to the hose barb on the vacuum flask. Place the Büchner funnel inside of the vacuum flask ensuring the rubber bung fits snug (air should not enter anywhere besides the porous plate at the top of the funnel). Using scissors cut the filter paper, 3 layers, to fit inside of the Büchner funnel. It is extremely important that the filter paper diameter be sized correctly. Unfiltered fuel may slip past the filter paper contaminating the filtered fuel. With the filter paper in place, pour a small amount of unfiltered fuel into the Büchner funnel. Then turn the

Figure 7 Filtering Apparatus
vacuum pump on. Keep the reservoir filled halfway with unfiltered fuel. Pay close attention to the level of filtered fuel inside of the vacuum flask. *IT IS IMPERATIVE THAT THE FILTERED FUEL LEVEL REMAIN BELOW THE VACUUM INLET; IF FUEL GETS INTO THE VACUUM PUMP DAMAGE MAY OCCUR.* Turn the pump off when the fuel level reaches 250ml. Remove the Büchner funnel and pour the filtered fuel into a clean labeled container. Repeat until all fuel is filtered.

Figure 8 Georgia Southern University Washed-Dried-Filtered Biodiesel

**Viscosity and Shear Stress Analysis of Test Fuels**

Viscosity is a measure of a fluid’s resistance to flow. Assemble the Model S Laboratory Stand. Put the viscometer on the stand. Viscometer must be leveled. The level is adjusted using the two leveling screws on the base. Adjust so that the bubble level on top of the DV-II Pro+ is centered within the circle. *Check level periodically during use!!!! Remove the white shipping cap which secures the lower coupling nut on
the Viscometer to pivot cup. Make sure that the AC power switch at the rear of the Viscometer is in the OFF position. Connect the power cord to the socket on the back panel of the instrument and plug it into the appropriate AC line. Turn the power switch to the ON position and allow to warm up for 10 minutes before performing autozero.

Turn the power switch to the ON position. After a short time, the display will read remove the spindle and press any key. Remove the spindle and press any key. *Spindle and Pointer Shaft are delicate and must NOT be bent!!!! Hold the pointer shaft between thumb and index finger and gently press upward. Gently hold the spindle between thumb and index finger and turn to the RIGHT to loosen. (To attach spindle to pointer shaft turn to the LEFT, DO NOT OVER TIGHTEN!!!!) After approximately 15 seconds, the display will read replace the spindle and press any key. Carefully reattach the spindle to the pointer shaft. Press the SELECT SPINDLE key, this will display the current spindle code selected and the S will blink. Press the UP or DOWN arrow to scroll to the desired code for the spindle selected. Once the desired code is selected press the SELECT SPINDLE key accept the new spindle code. Press the ARROW key once and release. The characters “RPM” will blink and display the currently selected speed. Press the UP or DOWN arrow key to change the RPM to the required speed. Press the SET SPEED key to accept the selected speed. Press the MOTOR ON/OFF/ESCAPE key to start the motor. Attach the mounting channel to the viscometer by threading the upper mounting screw into the viscometer pivot cup. Do not over tighten. The end of the mounting channel with pin must be at the bottom. Remove the water jacket from the “open tube”. Snap tube end cap over the bottom end of the sample chamber. Fill tube with 16 mL of fluid.
over fill. Place ULA spindle into the tube. Do not bend spindle neck. Attach tube to the clamping collar by aligning the pin with the pin groove and tightening the bottom mounting screw. Do not over tighten. Carefully attach spindle to pointer shaft. Note left hand thread. Do not over tighten. Level Viscometer. Attach the mounting channel to the viscometer by threading the upper mounting screw into the viscometer pivot cup. Do not over tighten. The end of the mounting channel with pin must be at the bottom. Fill tube with 6.7 mL of test fluid. Do not over fill. Place SC4-18 spindle into the tube. Do not bend spindle neck. Attach tube to the clamping collar by aligning the pin with the pin groove and tightening the bottom mounting screw. Do not over tighten. Carefully attach spindle to pointer shaft. Note left hand thread. Do not over tighten. Level Viscometer. Read and follow setup methods in sections IV-VIII. Start viscometer in lowest RPM setting. If torque readings under 10% are inaccurate, increase RPM to next increment. If torque becomes too great EEE will be displayed for torque and viscosity. Record the temperature of the fluid and the viscosity in the excel spread sheet using correct identification code.

**Determination of Energy Content Using a Constant Volume Calorimeter**

First, the bucket, capacitor, and temperature data logger (Figure I) must be plugged into an electrical source. Then, the electrode wires from the capacitor are plugged into the side of the bucket. Next, open Logger Pro software and plug the temperature data logger into a USB port on the computer. Figure II shows a display of the initial setup.
Make a pellet of benzoic acid weighing approximately 0.5g. **DO NOT USE AT TABLET OR SAMPLE OVER 0.8 grams!!!** Place pellet in crucible. Cut a 10 cm length of fuse wire and weigh it. Connect the wire to the electrodes on the calorimeter’s cap, keep wire from touching itself or the crucible and slightly away from the tablet/sample. Assemble the calorimeter and pressurize with oxygen to approximately 25 atmospheres. **WARNING DO NOT FILL OVER 40 ATM!!!** Pour in exactly 2kg of distilled water using weights and triple beam balance. Place water jacket in the bucket and place constant volume calorimeter in the water jacket. **Be sure to shake off any excess water, to reduce error in calculations** Stir water in the calorimeter, after about 2 minutes start taking the temperature readings for at least 5 minutes. Discharge the

Figure 9 Vernier data logger

Figure 10 Constant volume calorimeter setup
capacitor exactly 30 seconds after the previous reading, and release the ignition switch when the red light goes out. Record the temperature 30 seconds after ignition and then every 30 seconds while the temperature is on the rise. After a maximum temperature is observed continue to take temperature readings for a further 5 minutes, reverting to one minute intervals. Open the bucket, take out the calorimeter, release the pressure and open the calorimeter. Remove the unburned wire and weigh it (DO NOT weigh iron-oxide pellets, just the unburned wire). Calculate the amount of burnt wire.

Graph the results of a single test as three separate lines on the same scatter graph of Temperature vs. Time. (Pre-ignition, Combustion, Post Combustion). Apply a linear trend line to the pre-ignition and post combustion data. Display the equation for each line on the graph. Determine the maximum temperature difference (rise) during the combustion phase by subtracting the highest temperature reached during combustion minus the minimum temperature reached during combustion. Calculate the 63% rise value by multiplying the temperature difference by (.63) and then adding that value to the minimum temperature reached during combustion. Apply the 63% rise temperature to
the pre-ignition and post combustion linear trend lines (replace the x value with the 63% rise temperature) to determine the corrected $T_{\text{initial}}$ and $T_{\text{final}}$, then calculate the corrected temperature change using the corrected values.

Heat Capacity of Constant Volume Calorimeter ($C_{\text{v}}$) = \((\text{mass of pellet} \times \text{energy content of pellet} + \Delta \text{mass of wire} \times \text{energy content of wire}) / (\text{corrected temperature change})\)

Heat Capacity of wire = \((\Delta \text{mass of wire} \times \text{energy content of wire}) / (\text{corrected temperature change})\)

Specific Heat of Combustion ($H_{\text{g}}$) = \((\text{corrected temperature change}) \times (\text{calorimeter heat capacity} + \text{wire heat capacity}) / \text{mass of sample}\)

Find accepted values and compare to experimental.

Known Values used in calculations:

Specific Heat of Combustion of Benzoic Acid: 6318.4 cal/g = (energy content of benzoic acid pellet)

Specific Heat of Combustion of Wire: 1400 cal/g = (energy content of wire)
Chapter 4

Application

Influencing Factors on Full Bodied Methyl Ester Properties

The development of the database that would provide a basis for setting realistic specification values for biodiesel determined from expected contaminants in terms of the engine life and performance and present data to justify a particular specification value. The contaminants to be considered include water, free glycerin, bound glycerin, alcohol, free fatty acids, soaps, and residual catalyst. Later on, unsaponifiable matter, microorganism, and oxidation products were added. The reason for this was that a serious problem developed because it has been found that different researchers, running the same standardized tests on biodiesel, have obtained very different results. Like, until recently, that the cetane number of methyl soyate, a particular form of biodiesel often called, was believed to be about 48 and now new data has been presented, the cetane number may actually be as high as 60. This change goes well beyond measurement error, but probably attributable to fuel contamination.

The American Society for Testing and Materials maintains the standard for petroleum-based diesel fuels, which it covers three grades of diesel fuel: Grade No. 1-D, Grade No. 2-D, Grade No.4-D. Grade No.1-D is a light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds as in light trucks and buses, as well as a blending agent during the winter to improve diesel fuel cold flow properties. Grade No.2-D is a middle distillate fuel for applications that do not require a high volatility fuel, most commonly used in trucks and agricultural equipment. Grade No.
No 4-D is a heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel.

The results section of the report had 7 sections: unsaponifiable matter, water, free glycerin, bound glycerin, alcohol, free fatty acids, soap, and catalyst, oxidation of biodiesel. The unsaponifiable matter may have no harmful effects on engine performance except possibly for a change in the crystallization onset temperature caused by polar sterols. Unsaponifiable matter was measured by the AOCS Official Method Ca 6a-40. Crystallization properties were by the cloud point (ASTM Standard Method D2500), pour point (ASTM Standard Method D67) and the crystallization onset temperature ($T_{co}$) determined by differential scanning calorimeter (DSC) analysis. The crystallization was determined as the end point of the highest melting transition peak, that is, the lowest temperature at which the sample was completely liquid. The effect of unsaponifiable matter on the cetane number of diesel fuel and methyl soyate had slight changes in cetane number that are generally less than the 0.7-0.8 ASTM repeatability specification for cetane number, which are always less than the 2.6-3.1 reproducibility specification.

Water is a major source of fuel contamination and virtually all diesel fuel storage tanks can be assumed to contain some water. Water in the fuel causes two problems, corrosion of the engine fuel system components and microbial growth. In order to investigate this problem of water contamination, the solubility of water in methyl esters were measured and compared with diesel fuel. The primary problem came from the free water being microbial growth, the tendency of the methyl esters to support microbial growth was investigated. It was investigated by comparing the solubility of water in
methyl esters, 20% esters/80% No.2 diesel fuel blends, and No. 2 diesel fuel and to
determine the effect of oxidation level on the solubility of water in methyl esters.

There was a test that was conducted as part of the study that compared the
solubility of water in methyl esters with its solubility in diesel fuel. One of the results for
diesel fuel had a very low water content at the start of the experiment, about 28 ppm, and
no increase was observed after 18 hr of vigorous mixing. The difference between the
values reported for the solubility, 28 ppm, 81 ppm, and 30 ppm are not considered to be
statistically significant. One advantage of biodiesel is that it’s biodegradable, however,
this biodegradability may allow biodiesel to be more susceptible to microbial
contamination than petroleum fuels. Dirt samples were taken from a methyl soyate
storage site and were inoculated into a liquid media containing various nitrogen sources,
and carbon sources, and the microbial growth was compared. They were incubated on a
shaker in the dark at room temperature, and their growth was monitored by measuring the
optical density of the aqueous phase of the culture media with a spectrophotometer. The
increase in the activity of microorganisms on biodiesel, especially molds, is also reason
for concern.

Free glycerin is a product from the transesterification reactions and is not present
when esters are washed thoroughly with water, but glycerin may be present in biodiesel
as a result of inappropriate processing. It’s solubility in methyl esters is low, free glycerin
tends to collect, over time, at the bottom of storage tanks. Bound glycerin is collectively
monoglycerides (MG), diglycerides (DG), and triglycerides (TG) compounds. There are
two reasons for keeping the amount of bound glycerin low and the first is if the bound
glycerin is in solution and is injected into the engine, there is suspicion that it will cause carbon deposits on the fuel injector tips and piston rings. The second reason for controlling the amount of bound glycerin is that the partially reacted glycerides, particularly the saturated MGs, have very low solubility in methyl esters and require high temperatures to keep them from crystallizing. Diglycerides are generally observed to have lower crystallization temperatures than MGs. Diglycerides have been reported to inhibit or retard the phase transition of triglycerides.

Methyl alcohol is the most common alcohol used for producing biodiesel, but ethanol is used in some cases. If the biodiesel is washed with water when the transesterification reaction is complete, there should be very little alcohol left since the alcohol is more soluble in the water than in the biodiesel. Also, if it is vacuum dried to remove the residual water from the washing operation, any remaining methanol should be removed. Free fatty acids, soap, and catalyst are treated together because they are related compounds. An alkaline catalyst such as sodium methoxide, sodium hydroxide, or potassium hydroxide is used to produce biodiesel. The primary problem with these contaminants is that when the fuel burns in the engine, the metal remaining from the soap or catalyst will be converted to ash.

**Modeling Cetane Number of Neat and Composite Methyl Esters**

In a previous study the cetane numbers were determined with the Ignition Quality Tester (IQT). The cetane number (CN) is a dimensionless descriptor for the ignition delay (ID) time of a diesel fuel upon injection into the combustion chamber. In other words, a widely used diesel fuel quality parameter related to the ignition delay time (and
combustion quality) of a fuel and has been applied to alternative diesel fuels such as biodiesel and its components. The basic concept of the IQT is measurement of the time from the start of fuel injection to the combustion chamber to the start of combustion.

The high cetane standard is CN=100, n-hexadecane, and the first CN in history with a high CN was carried out on palm oil ethyl esters. The low cetane standard is CN=15, 2,2,4,4,6,8,8-heptamethylnonane. For mono-alkyl esters, low CNs were linoleic and linolenic acids which had long ID times and subsequent poorer combustion associated with more highly unsaturated components. Whereas high CNs being palmitic and stearic acids were saturated fatty acids. Another CN which was medium range and a mono-unsaturated acid was oleic acid.

Freedman et al. obtained a quadratic equation correlating the CN of saturated FAME with the carbon number as follows:

\[ Y = -57.26 + 14.892X - 0.4149X^2 \]

where \( Y \) is the CN, and \( X \) is the carbon number of fatty acid chain.

Lapuerta et al. also developed a correlation between the CN of pure FAME and the carbon number as well as the number of double bond in the following equation:

\[ Y = -52.974 + (13.767 \cdot 1:202db + 0.152db^2) - 0.351X \]

where \( Y \) is the CN, \( db \) is the number of double bonds and \( X \) is the carbon number.

Bangboye et al. suggested a regression equation described as follows:

\[ CN = 61.1 + 0.088x2 + 0.133x3 + 0.152x4 - 0.101x5 - 0.039x6 - 0.243x7 - 0.395x8 \]
where \(x_2\) to \(x_8\) are the weigh percentages of methyl myristate (C14:0), palmitate (C16:0), palmitoleate (C16:1), stearate (C18:0), oleate (C18:1), linoleate (C18:2) and linolenate (C18:3) in biodiesels, respectively.

Gopinath et al. also developed a multiple linear regression model as the following equation:

\[
CN = 62.2 + 0.017L + 0.074M + 0.115P + 0.177S - 0.103O - 0.279LI - 0.366LL
\]

where \(L, M, P, S, O, LI\) and \(LL\) are the weight percentages of methyl laurate (C12:0), myristate (C14:0), palmitate (C16:0), stearate (C18:0), oleate (C18:1), linoleate (C18:2) and linolenate (C18:3) in biodiesels, respectively.

(Saturated only) The CN was given as the dependent variable \(Y\), while the carbon number of fatty acid chain was given as variable \(X\). The fitted curve is a cubic polynomial described as the following regression equation:

\[
Y = -107.71 + 31.126X - 2.042X^2 + 0.0499X^3
\]

(Dongmei Tong, 2010)

The nonlinearity can be described as the following quadratic equation:

\[
Y = 109.000 - 9.292X + 0.354X^2
\]

where \(Y\) is the fitted CN and \(X\) is the carbon number of unsaturated fatty acid chain containing one carbon–carbon double bond. (Dongmei Tong, 2010)

Correlative Model

\[
CN = 1.068 E(CNiwi) - 6.47
\]

where \(CN\) is the predicted CN of biodiesel, \(CNI\) is the CN of each pure FAME as shown in Table 1, \(wi\) is the weight percentage of each FAME in biodiesel as independent variable of regression equation. (Dongmei Tong, 2010)
This indicates that the present correlative model is a simple and practical method to give a satisfactory predicted CN of a biodiesel from its FAME composition without arduous and expensive experimental determination. (Dongmei Tong, 2010)

Therefore, for calculation of the HHVs (MJ/kg) of oil samples, Eq. 4.16 was suggested (Demirbas, 1998).

\[ \text{HHV} = 49.43 - 0.041 \text{ (SV)} - 0.015 \text{ (IV)} \] (4.16)

SV=saponification value

IV=iodine value

(Demirbas, 2009)

Variation of % DCN increase with % FAME lost during oxidation (Kapila Wadumesthrige, 2008)

\[ Y = 2.655X + 8.413 \]

Y=% DCN increase

X=% FAME composition lost

**Effects and Solutions to Poor Oxidative Stability of Biodiesel**

The iodine value, expressed as grams of iodine absorbed/100 g sample, represents a description of the unsaturation of oils and their fatty acid derivatives, and was determined directly from fatty acid compositions and corresponding acid factors given in the standard method. Acid factors are the reacting ratios of I\(_2\) to the individual fatty acids. The unprocessed grease methyl ester had the lowest iodine number, followed by the processed grease methyl ester, the green seed methyl ester, and the canola methyl ester.
These data show that the canola and green seed methyl esters have a greater degree of unsaturation than the processed and unprocessed. (S.L. Dmytryshyn a, 2004)

The technological problems associated with biodiesel, are the oxidative stability, poor low-temperature properties, and a slight increase in NOx emissions, especially from biodiesel derived from vegetable feedstock, even though the NOx issue may be solved with the introduction of innovative exhaust emission control technologies. This behavior is connected to the reliance of fuel properties on the fatty acid composition. As a result of the relatively large number carbon molecules of biodiesel versus diesel, the biofuels are susceptible at low temperatures to separate and crystallize, resulting in a higher cloud point. This occurrence of solid crystals in the fuel increases the viscosity and the passage of the fuel through the fuel filter. It has been revealed also that the Cetane number, decreases with a decreasing chain length, and an increasing unsaturation in the fatty acid chain. However saturated esters, which have high and therefore desirable, cetane numbers, are characterized by poor cold-flow properties. Unsaturated, in particular polyunsaturated, fatty esters have lower melting points, which are desirable for improved low-temperature properties but also have lower cetane numbers and reduced oxidative stability, which is detrimental for a fuel.

There are several approaches that have attained common practice to alleviate these issues. One of the most common approaches is to use of additives, such as antioxidants, cetane enhancers, or cold-flow improvers. Another solution is the production of biodiesel from an alcohol other than methanol forming ethyl and isopropyl esters which display improved low temperature properties without reducing cetane
number or oxidative stability. The problems associated with this method are the significantly increased cost of production as well as modifications required of the transesterification process. A fourth approach, and the one of most interest to this study, is the use of bio-oils with reformulated fatty acid compositions that provided the biofuels with improved properties. Respectively, oleic FAME has been recommended as the leading component of such doped biodiesel. This method, would address both the technical issues related with biodiesel use without adversely affecting other properties, as with the use of alcohols other than methanol. A recent preliminary discussion, on the topic of altering the esterified fatty acid composition of biodiesel was opened. Additional options to oleic FAME include esters of palmitoleic acid, saturated short-chain esters, hydroxyl containing esters, and esters other than methyl.

The use of esters other than methanol and physical procedures, such as winterization, improve cold flow, with economics being an issue when using alcohols and reduced oxidative stability and cetane numbers being issues in the case of winterization. For biodiesel, methyl palmitoleate and esters of decanoic acid are strong candidates for improving fuel properties besides methyl oleate, but several other issues, however, will be likely need to be evaluated when considering such modified feedstocks and fuels. (Knothe, 2008).

**Determination of Residual Contaminants in Biodiesel**

The amount of soap and residual catalyst in the methyl soylate was determined by adding a sample of the wash water to a larger quantity of ethanol and titrating with 0.01N
HCl using a phenolphthalein indicator solution. The amount of residual catalyst was calculated from the formula:

\[
\% \text{ Catalyst (as potassium hydroxide)} = \left( \frac{Q_1 \times 56.1}{1000g} \right) \times 100
\]

Where \( Q_1 \) = milli equivalents of 0.01N HCl added.

\( Q = \) sample size in grams

The amount of soap was calculated from the formula:

\[
\% \text{ Soap (as sodium oleate)} = \left( \frac{Q_2 \times 304.4}{1000g} \right) \times 100
\]

Where \( Q_2 \) = milli equivalents of additional 0.01N HCl added.

**Biofuel Doping**

The use of dopes may be considered to be one of the most promising methods for improving the ignition quality of diesel fuels and their use may make it possible to meet special requirements with respect to a high cetane number combined with a low cloud and pour-point of the fuel. The use of low-boiling fractions seems to make an exception, which has the disadvantage of greatly reducing the output of suitable fuel and the risk of involving too low a viscosity for diesel engine practice. For a pour point below -40°F, one has to start usually with fuel of cetane number 30-35. A minimum of 2.5-3% by weight of even the most effective dopes would hence to be added to bring the cetane number up to specification, which will call for an increase of some 20-25 cetane numbers to meet such a special fuel requirement. The most efficient way would be to start from fuels with a low pour-point which may be extracted to give cetane numbers up to 40, and then to add 1-1.5% dope.
A dope for the improvement of the ignition quality of a fuel has to fulfill the following requirements:

a) It must be as effective as possible;
b) It must be soluble in the fuel up to high concentrations;
c) It should not be soluble in water;
d) It should not be influenced by acidic components in fuels (unless the fuel be previously soda treated);
e) It must have a high degree of stability in storage
f) It must not be explosive under moderate temperature conditions when in solution
g) Its manufacture, yielding a constant product, should be reasonably easy
h) It should not have corrosive
i) It should be inexpensive

It should be clear that all requirements cannot be fulfilled to the same degree without influencing each other. A great number of diesel dopes were mentioned, but only a few of them fulfill the above requirements in a satisfactory way. In the paper the authors discussed their results obtained with acetone peroxide and ethyl nitrate as dopes, and mainly with respect to: their influence on the ignition delay of a fuel, the further stages of the combustion process, wear and incrustations in the engine, and various subjects, as storage tests, etc.

For the influence of a dope on the ignition delay of a fuel, very little is known about the effects of a dope on the chemical processes occurring during the ignition period. Experimental results of the effect of a dope on the ignition delay will be discussed
with respect to the dependence on: the chemical activity of the undoped fuel, the physical delay of the fuel, and the engine conditions. For the chemical activity of the undoped fuel, the first effect was expressed in the decrease of the ignition delay, is greater in a low cetane fuel than in a high cetane fuel. Secondly, comparing two fuels of equal cetane number, one undoped and the other doped and further adding equal amounts of dopes to both fuels, then the effect of this dope addition is greater on the undoped than on the doped fuel. Thirdly, the effect of a dope, expressed either as an increase in the cetane number, or as a decrease of the ignition delay, decreases the more dope has already been added to the fuel.

For the physical delay of the fuel, with light distillate fuels many experiments have shown that this physical delay is usually very small with respect to the total delay. In heavy fuels the physical delay, the effect of a dope will then become relatively less great. The chemical nature of peanut oil is such that a short chemical delay can be expected. For engine conditions, in high speed engines the value $\varepsilon$ in the formula for the reaction velocity will be greater than in lw speed engines. However a lower effect of a dope, expressed in delay time, in a high speed (hot) engine than in a low speed (cold) engine.

For the effect of a dope on the combustion process, there are four stages of the combustion process, introduced by Ricardo: stage 1 ignition delay, stage 2 combustion of the fuel injected during stage1, stage 3 ignition and combustion of fuel injected later and stage 4 after burning. It has not yet been possible to detect clearly an influence of the chemical composition of the fuel on the combustion process, apart from the influence
determined by the ignition quality. An effect of dope addition to a fuel on the combustion process as a whole may be expected only in the shape of an effect on ignition quality. The more so when the small percentages are considered in which dopes are added to a fuel. Differences in the diagrams for the undoped and doped fuels of practically equal cetane number can scarcely be found. (Broeze, 1939)

Restrictions on the FA profile. The reason for restrictions on the fatty acid (FA) profile, contained mainly in EN 14214, is to exclude components of biodiesel with less desirable properties, for example, with respect to oxidative stability. In practice, this can amount to excluding certain feedstocks for biodiesel production. The content of methyl linolenate is restricted in EN 14214 because of the propensity of methyl linolenate to oxidize. However, the limit (12%) is set so as not to exclude high-oleic rapeseed oil, the major biodiesel source in Europe, as feedstock. The iodine value (IV) is a measure of total unsaturation of a lipidic material. An upper limit of 5 mm²/s for kinematic viscosity in biodiesel standards may exclude some frying oils as feedstock. Biodiesel fuels derived from used frying oils tend to possess higher viscosity than those from most vegetable oils, owing to their higher content of trans FA and saturated, or, more generally speaking, less unsaturated FA. The acid value, like kinematic viscosity, is a facile method for monitoring fuel quality. The flash point specification serves to restrict the amount of alcohol in the biodiesel fuel. The sulfated ash test (ASTM D 874 in ASTM D 6751; ISO 3987 in EN 14214) is designed for determining sulfated ash from lubricating oils containing various metal-containing additives. The carbon residue test (ASTM D 4504 in ASTM D 6751; ISO 10370 in EN 14214) is designed to indicate the coking tendency of
the sample. The amount of carbon residue formed after evaporation and pyrolysis of the weighed petroleum sample is determined. Calcium and magnesium are of concern for soap formation. They may also be found in animal fats as a result of contact with nonlipidic material. Sulfur, like phosphorus, is a potential catalyst poison. The specification is important to show that biodiesel will not negatively affect automotive catalyst systems. The copper strip corrosion test (ASTM D 130 in ASTM D 6751; ISO 2160 in EN 14214) consists of dipping a strip of copper into the fuel for a specified time and defined temperature and observing the corrosive action of the fuel. It is a test for corrosive sulfur compounds in the fuel. Traces of phosphorus, resulting from phospholipids, can remain in vegetable oils after refining. Phosphorus can poison catalysts used for reduction of exhaust emissions. The cetane number is a dimensionless descriptor of the ignition quality of a diesel fuel. It is related to the ignition delay time a fuel experiences on injection into the combustion chamber. Cloud point and cold-filter plugging point (CFPP). ASTM standard D 6751 prescribes the use of the cloud point standard reference method D 2500 for assessing the low-temperature properties of biodiesel. No limit is given; rather a “report” is specified. The reason is that the climate conditions in the United States vary considerably and therefore the needs of biodiesel users vary accordingly. A density specification is contained in the European standard EN 14214. The purpose is to exclude extraneous material as biodiesel feedstock. Water in the sample can promote microbial growth, lead to tank corrosion, participate in the formation of emulsions, as well as cause hydrolysis or hydrolytic oxidation. (M. Canakci, 2001)
Chapter 5

Experimental Setup

The Engine Used for Combustion and Emissions Analysis of Biofuels

The engine used in this research is made by Kubota, model EA-330 and it is a single cylinder, CI, naturally aspirated engine with a horizontal power take-off (PTO) shaft. (Figure 11). The engine has a max RPM of 3000, is advertised to produce 17.7 Nm of torque and 5.15kW of power. (Figure 14 & 15)

Figure 11 Kubota EA330 Model Engine (KUBOTA Corporation 2008)
<table>
<thead>
<tr>
<th>Model</th>
<th>EA330-E3-NB1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Emission Regulation</td>
<td>Tier 4</td>
</tr>
<tr>
<td>Type</td>
<td>Horizontal 4-cycle liquid cooled Diesel</td>
</tr>
<tr>
<td>Number of Cylinders</td>
<td>1</td>
</tr>
<tr>
<td>Bore mm (in)</td>
<td>77 (3.03)</td>
</tr>
<tr>
<td>Stroke mm (in)</td>
<td>70 (2.76)</td>
</tr>
<tr>
<td>Displacement L (cu.in)</td>
<td>0.325 (19.83)</td>
</tr>
<tr>
<td>Combustion System</td>
<td>IDI (TVCS)</td>
</tr>
<tr>
<td>Aspiration</td>
<td>Naturally Aspirated</td>
</tr>
<tr>
<td>Maximum Speed rpm</td>
<td>3000</td>
</tr>
<tr>
<td>Output: Net Intermittent kW</td>
<td>5.15</td>
</tr>
<tr>
<td></td>
<td>HP</td>
</tr>
<tr>
<td></td>
<td>PS</td>
</tr>
<tr>
<td>Oil Pan Capacity L (gal)</td>
<td>1.3 (0.34)</td>
</tr>
<tr>
<td>Starter Capacity V-kW</td>
<td>12.0-8</td>
</tr>
<tr>
<td>Alternator Capacity V-A</td>
<td>12-3.5</td>
</tr>
<tr>
<td>Length mm (in)</td>
<td>566 (22.28)</td>
</tr>
<tr>
<td>Width mm (in)</td>
<td>411 (16.18)</td>
</tr>
<tr>
<td>Height (1) mm (in)</td>
<td>457 (17.99)</td>
</tr>
<tr>
<td>Dry Weight kg (lb)</td>
<td>54 (119)</td>
</tr>
</tbody>
</table>

Figure 20 Specification Sheet for EA-330 Kubota Engine (KUBOTA Corporation, 2008)
Figure 12: Power, Torque, and Fuel Consumption vs. Speed (KUBOTA Corporation, 2008)
Hydraulic Dynamometer Used for Load Application

For the engine testing in the laboratory, a pump dyno was used to mount the Kubota EA-330 diesel engine to a table top and have the PTO shaft of the motor drive a pump by sprockets and chains. This pump pumps hydraulic oil through hoses with a “T” shape connector that is attached to a pressure gauge, then oil is pumped through a needle valve, and then into a tank where the oil was first gathered; therefore creating a closed circuit. The set up of the dyno is that the engine turns the pump, the pump pumps oil through the system, the pressure gauge reads the pressure in the lines, and the needle valve controls the pressure in the lines. This system enables the dyno to place a resistive load on the motor by means of the pump being connected to the engine and through a few formulas, the power and torque at the pump can be determined.

The engine has a PTO shaft with a 22 tooth, #16 chain sized sprocket attached. This sprocket drives a chain which connects to the pump on the dyno by means of another #16 size sprocket, but with 55 teeth; therefore giving the engine to pump ratio of 0.4. The pump will be turning at 40% the rate of the engine, and the torque will be 2.50 times greater on the pump shaft then on the engine shaft due to the larger diameter of the sprocket. As mentioned before, the purpose of the dyno is to be able to apply resistive loads to the engine so as to simulate load.

After the dyno is assembled, some calculations can be completed. Through a few formulas the amount of power and torque required to turn the pump at a given rpm and resistance can be determined. The assumption is that the power required to turn the pump
is the same amount of power the engine is producing; therefore the chain system can be isolated and the pump considered to be mounted directly to the engine.

**Calibration of Dynamometer Used for Testing.**

There were some problems that arose during the initial setup. The engine and the pump have a maximum rotation speed of 3000 rmps and the pressure gauge and hoses only allow 3000psi, and it is desired to not exceed the maximum allowable pressure, yet still maintain a wide range of loads before the engine is stalled by overloading. With a pump displacement estimated to be 1.4 in$^3$/rev, it would not take much turning of the needle valve to max out the hoses, the gauge, and the engine itself.

One desired feature is that the load on the engine be known at any given point in time with the known parameters of rpm and pressure in the system. This can be solved by the formulas provided by the dyno table manufacturer.

\[
HP_{pump} = \frac{PSI \times GPM}{1400} \tag{1}
\]

Where \(HP\) is the power in terms of horsepower, \(PSI\) is the pressure in the dyno system given in lbs/in$^2$, and \(GPM\) is the flow rate given in gallons/minute. The number 1400 is a constant to determine the US standard unit of power, which is horsepower.

\[
Torque_{pump} = \frac{HP_{pump} \times 5252}{RPM_{pump}} \tag{2}
\]

Where \(HP\) is the power determined from Equation 1, 5252 is a constant used to determine the US standard for torque, which is \(lb \times ft\), and \(RPM\) is the revolutions per minute of the pump. Also, a simple conversion factor can be used to convert these units to metric units.
Through Equations 1 and 2, a load on the engine can be determined at any given time. The mean effective pressure (MEP) needs to be determined because this is an accepted method for comparing engines and using different MEP levels as benchmarks for testing engines. The MEP is given by:

\[
P_{mep} = \frac{T n_c}{V_d} \frac{2\pi}{2\pi}
\]

Where \( T \) is the torque, \( n_c \) is the number of revolutions per cycle (for a four stroke engine, the answer is 2), and \( V_d \) is the volumetric displacement of the engine. The pressure required for desired MEP is determined by manipulating Equations 1 through 3:

\[
PSI = \frac{P_{mep} V_d N_{pump} Unit \ Conversion_1}{2\pi Q Unit \ Conversion_2}
\]

Where \( N_{pump} \) is the pump revolutions in revs per minute, \( Unit \ Conversion_1 \) is the conversion factor for torque in metric units (Nm) and mentioned in Equation 2, \( Q \) is the flow rate of the pump in GPM, and \( Unit \ Conversion_2 \) is the conversion factor for power in metric unit kilowatts (kW) as mentioned in Equation 1.

**Determination of Load Application By Efficiency of Hydraulic Pump.**

Equation 4 is used to determine the amount of pressure needed to produce a given MEP with the known pump revolutions and flow rate. Equation 4 also shows that the pressure in the dyno system is dependent upon pump speed and the desired MEP and the
flow rate; this may be true, however, the only factor that needs to be controlled when wanting to apply a desire MEP load to an engine is the pressure.

Bernoulli’s equation is defined as follows:

\[
\frac{\Delta p}{\gamma} + \Delta Z + \frac{\Delta \vec{V}}{2g} = h
\]  

(5)

And the flow rate equation is:

\[
\dot{Q} = \vec{V} \cdot area
\]  

(6)

Where \( \dot{Q} \) is the flow rate, and \( \vec{V} \) is the velocity and Area is the area of the hoses. Note that these are dependent upon one another, so if flow rate increases, and area stays the same, then the velocity must increase in order to maintain the increase of flow rate.

Based on Equations 5 and 6, when the engine increases in speed, so will the pump, and the flow rate will increase, therefore causing the velocity of the oil to speed up to maintain the flow rate because the area of the hose is not going to change. This causes the pressure difference between the two flow rates, increasing the load on the engine. As a result, the engine has to work harder to push the fluid through the system, but the needle valve adjusts for this.

The area changes because of the needle valve which can be adjusted while the engine is running. If flow rate increases, the area of the needle valve can increase till there is no difference in the velocities from the flow rate change, and if there is no change
in velocity, then, according to Bernoulli’s equation, there is no pressure change, this results in no engine load change.

This allows a determined dyno pressure setting to correlate with incremental MEP settings regardless of engine speed; only the pressure needs to match the defined MEP setting as defined. (Table I)

<table>
<thead>
<tr>
<th>Dyno Pressure (psi)</th>
<th>MEP (Bar)</th>
<th>Torque (Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 240</td>
<td>1</td>
<td>2.59</td>
</tr>
<tr>
<td>2 480</td>
<td>2</td>
<td>5.19</td>
</tr>
<tr>
<td>3 720</td>
<td>3</td>
<td>7.78</td>
</tr>
<tr>
<td>4 960</td>
<td>4</td>
<td>10.38</td>
</tr>
<tr>
<td>5 1200</td>
<td>5</td>
<td>12.97</td>
</tr>
<tr>
<td>6 1440</td>
<td>6</td>
<td>15.56</td>
</tr>
<tr>
<td>7 1680</td>
<td>7</td>
<td>18.16</td>
</tr>
</tbody>
</table>
Dynamometer Conclusion.

The pump with the 1.403 in³/rev displacement enables the user to use the most range of the dyno, while maintaining safety factor of 1.5 and keeping accuracy in the pressure.

Dynamometer Cooling System.

The calibration of the dyno does not take into account the temperature of the dyno oil. As the engine is running, the dyno oil temperature rises which affects the load on the engine. The solution was to pump the hydraulic oil through an oil cooler that will dissipate enough heat to maintain the hydraulic oil as the desired range of 38-42 °C. This requires an oil cooler that can be controlled because there were different amounts of energy being absorbed by the oil. If the oil cooler is dissipating more heat than the oil is absorbing, then the oil temperature can drop below the operating range.

In line pressure gauges before and after the cooling systems determined the pressure change in the hoses due to the addition of the cooling system. The first cooling system was a car radiator with an electric fan was used to cool the oil; it succeeded in holding the proper temperature, but the pressure that was produced in the system was 4 times the normal radiator operating pressures. The radiator was the pressure producing problem because all of the fluid was spread across the many small fins of the radiator. Therefore, to reduce the pressure, a second radiator was added in parallel to the cooling system; the hydraulic oil was passing through two radiators at the same time. This also succeeded in holding the hydraulic oil temp within range, but again the pressure in the system was above the normal operating pressures for the radiators.
The solution to this was solved by a copper coil submerged in a tank with regulated water flowing through the tank to maintain temperature. (Figure 1) The copper tubing was chosen because its maximum allowable pressure is far beyond any pressure that will produced by the dyno. Also, copper is a great conductor of heat therefore making it well suited for cooling hot oil that will be passing through it. Lastly, it was made into a coil because the tubing was 60 feet long and needed to make a compact cooler that would be able to fit in a tank underneath the dyno table. The tank allows water to be introduced across the coil for fast heat transfer, but also, the amount of water flowing through the tank and across the coil was controllable which made it possible to control the dyno oil temp.

Figure 14 Cooling System for Dyno Oil

Crank Angle Measurement Using a Rotary Encoder

In order to measure the engine cycle, the angle of rotation and piston location are desired. The solution to this problem is to introduce a rotary encoder to the engine which will enable data collection of the engine cycle. But the solution of this problem
introduces another problem which will be discussed here. The problem then becomes that the encoder needs to be attached to the engine in a manner that the encoder will not be disturbed and still collect acceptable data.

**Rotary Encoder Background.**

Introducing a rotary encoder enables the measurement of the engines rotation cycle. A rotary encoder is an electro-mechanical device used to convert the angular position of a shaft or axle to an analog or digital code by emitting light from a light emitting diode (LED) and through a slotted disk and then picking up the light with a photo sensor, making it an angle transducer. (Figure 15)

![Figure 15 Basic Internal Parts of an Optical Encoder (Omron, 2010)](image)

The encoder used in this setup was an Omron optical rotary encoder with 2000 pulses/revolution for channels A and B, and 1 pulse/revolution for channel Z. (Figure 1) As the encoder rotates, the slotted disk rotates as well and as each slot passes by the LED, the light is picked up on the other side of the disk by a photo sensor, ultimately giving a pulsating signal that jumps from 0 to 5 volts in the form of a square wave: for channels A and B, the pulses are in an offset of 90°. (Figure 1)
The mounting of the rotary encoder is important for the proper operation of the encoder. The encoder is small when compared to the engine, and takes very little effort to rotate the shaft, but the encoder shaft needs to be attached to the PTO shaft of the engine where all of the power generated from the engine is transferred.

Mounting the encoder requires the alignment of the encoder shaft with the PTO shaft. The two shafts needed to remain concentric and parallel and still maintain a 1:1 ratio from shaft to shaft revolution. The only position available to mount the rotary encoder was to mount it to the flywheel cover of the engine with the use of a flange. This
position enabled the most stable, concentric, and parallel mounting capabilities while still offering small position adjustments if needed. The flange fabricated is shown in 19.

![Illustration of Actual Encoder Mounting](image)

**Figure 20: Illustration of Actual Encoder Mounting**

**Determination of Top Dead Center**

Once the encoder was mounted, the encoder needed to be synchronized with TDC of the engine. Channel Z of the encoder, one pulse/rev, needed to be lined up with TDC of the engine. There were several approaches and achieve the alignment of TDC with the index pulse.

**Mechanical Method.**

The first approach to align TDC with the encoder was the mechanical method; setting the engine at TDC according to the engine shop manual. (Figure) The flywheel of the engine has a mark, when aligned with the mark of the pulley cover; the engine is set
at TDC. This approach was taken, and then the encoder was attached, data was collected and the TDC alignment was studied.

Figure 21 (1) is the T-Mark and (2) is the Fan Cover Mark (KUBOTA Corporation, 2008)

**Compression Curve Method.**

Generally, TDC is in the center of the pressure curve of when the engine is motoring; this is when the engine is being rotated by the starter. (Figure 2) At this point the engine is going through all four cycles, except there is no combustion to perform the power stroke. However, due to piston ring leakage and heat transfer, the peak pressure position should occur before TDC. (Hsu, 2002)
Another way to align TDC was to base it off of the fuel injection timing which was defined as 27° BTDC. But after further investigation, this marking starts the fuel pressure being built up into the fuel lines and not the actual point where fuel is injected into the lines. This is known because of the general timing of diesel fuel injection which is around 13° BTDC, but also because of the known pressure required for the fuel injector to crack and begin injection. The Kubota manual describes the pressure required for the injector to crack is around 2000 psi, so when the fuel line pressure curve collected from the oscilloscope is obtained and the conversion factor applied, the point of injection can be determined and this resulted to be around 14° BTDC. (Figure 2)
In the research conducted, there was a pressure probe used in the cylinder head to measure the pressure throughout the engine cycles. The pressure inside of the combustion chamber will vary all throughout the engine cycle (Figure 24), and the time between the pressure differences are short. For example, the air and fuel is sucked down into the cylinder by the expansion of the piston in the cylinder creating a vacuum and the pressure is less than 1 atmospheric pressure. Following induction comes the compression stroke,
here pressure will increase based on the rate of engine rotation, but pressure will spike when combustion occurs. Continuing through the cycle, the power stroke will have high pressure through most of expansion due to combustion, but will drop at the end of the expansion based upon engine speed and combustion rate. Following the power stroke, the piston will begin to reach the bottom of its stroke and a couple things happen here: the change in pressure will be much lower than the other previous strokes and the time between the small pressure changes will be longer because of the piston spending a significant amount of time of the engines rotation where the cylinder pressure is relatively low because it is at the bottom of the stroke. Following the power stroke, the exhaust stroke happens as the piston begins its return to the top of the cylinder. This stroke pushes all of the burnt fuel, now in gas form, out through the exhaust, and even though the piston is on its up stroke, the pressure in this stroke is relatively constant because as it is compressing, the exhaust valve is open and allowing all of the gases to escape. The final stroke to occur is the intake and this is where the intake valve opens and air and fuel is allowed to enter the cylinder.
A pressure transducer was necessary to be able to measure the pressure ranges (Max=350 bar) and able to capture pressure changes in an appropriate amount of time. The pressure probe also needed to withstand the high temperatures that exist in the engine as temperatures will reach an excess of 2200 degrees Kelvin.

**Decision of Pressure Transducer.**

Most of the sensors offered required drilling and tapping into the cylinder head of the engine and mounting the sensor by screwing it in to a tapped hole. This method produced several problems: first problem was drilling into a cylinder head because there were no available drawings of the cylinder head. Drilling into cylinder head without
drawings is risky because of other components inside the cylinder head and possibility of damaging the sensor.

Another problem with drilling is the engine is water cooled and therefore has a water jacket running through the cylinder head. If a sensor was introduced by drilling and tapping, there would be access for water to escape through the sensor hole. To stop this from happening, Kistler provides rubber seals to fit around the outside of the pressure probe, which also help reduce vibrations and noise of the signal. If the probe is to be sealed, this requires material of the cylinder head to be present for seals to be effective. (Figure 27)

Due to the complexity of the cylinder head and no available drawings, drilling and tapping is complex and unlikely to be the acceptable option. (Figure 28)

Figure 25 Illustration of Pressure Probe Mounting Setup (KISTLER, 2003)
Figure 26 Cylinder Head Removed from Engine for Investigation of Pressure Probe Placement

Since drilling and tapping was unlikely, introducing the sensor through the glow plug hole was investigated. This option did not require any drawings because the hole was already in a position where it was not interfering with any water jackets. The glow plug hole is already drilled and tapped, and there was no obstruction of other cylinder head parts such as valves to get in the way. The glow plug could be removed and easily
measured in order to have a design for a sensor. And after further investigation, Kistler offered a glow plug adapter by which a specific sensor could be introduced into the adapter, given the adapter dimensions, and be able to measure the pressure inside the combustion chamber. (Figure 27)

![Diagram of Pressure Sensor, Glow Plug, and Adapter]

Figure 27 Advertised Glow Plug Adapter for Pressure Probe (KISTLER, 2003)

This glow plug adapter solved many problems that had previously been encountered, however it introduced new problems. The depth of the sensor still had to be at appropriate length so that the tip of the sensor would not be hit by the piston as it is in the upward stroke. If the sensor was too long, the tip would break and destroy the sensor. To accommodate this problem, the existing glow plug had to be measured accurately. To achieve this, two methods were used: measuring the glow plug by hand with a caliper and retrieving drawings of the glow plug from the manufacturer. If the glow plug adapter for the pressure sensor can match the glow plug dimensions, then no problems should arise.
Additional Issues Addressed.

A diesel engine combusts fuel by compression and combustion cannot occur if the surrounding temperatures are too cold. To solve this problem, a glow plug is introduced to heat up the combustion chamber by having electrical power sent to the glow plug; it then heats up the surrounding air. With the glow plug replaced by a pressure sensor, the heating element is no longer available.

The solution to the problem with removing the glow plug is that the engine will be ran indoors in a laboratory with room temperature (20-25°C). This will eliminate any need for a glow plug for cold starting. However, this leaves the problem with the temperatures required for the bio-diesels to self ignite without a glow plug.
Calibration of Pressure Transducer.

The pressure transducer was shipped in a “ready to use” form, and therefore required no calibration of the sensor itself; however, the transducer requires a charge amplifier with multiple settings that need to be established. The way in which the piezoelectric pressure transducer works needs to be discussed in order to explain the following explanation of the calibration.

A piezoelectric sensor involves a crystal that undergoes a piezoelectric effect defined as the property of a crystal to exhibit electrical charges under mechanical loading and considered to be active electrical systems. They only exhibit an electrical charge output when it experiences a load change; therefore, without some type of signal conditioner, static forces cannot be measured. But pressure inside of a combustion chamber during engine operation is constantly changing therefore making a piezoelectric transducer adequate for this study because it is suited for measuring rapid dynamic phenomena and is best in engine pressure measurement. Also, the electrical output of the crystal is in the form of a charge (coulombs), therefore a charge amplifier that converts the small charge output from the mechanical loads applied to voltage. The charge amplifier linearizes the conversion from charge to volt for the ease of converting electrical signals to a mechanical force. This is all done by use of the charge amplifier with complimentary settings for the transducer being used. (Figure 32-33) Those settings are established in Table IV-VI.
Figure 29 Kistler Charge Amplifier

Figure 30 Pressure Probe Schematic for DAQ
Table II: Settings used for Charge Amplifier and the Corresponding Reasons

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
<th>Units</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transducer</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sensitivity</td>
<td>22.3</td>
<td>pC/MU or</td>
<td>*Sensitivity setting matching desired parameters from calibration sheet</td>
</tr>
<tr>
<td></td>
<td></td>
<td>mV/MU</td>
<td></td>
</tr>
<tr>
<td>Scale</td>
<td>10</td>
<td>MU/Volt</td>
<td>**Ease of conversion and also fits within the range of amplifier voltage output</td>
</tr>
<tr>
<td>Time Constant</td>
<td>Medium</td>
<td>-</td>
<td>Recommended for engine applications</td>
</tr>
<tr>
<td>Mode</td>
<td>Charge</td>
<td>-</td>
<td>Required mode for 6056A pressure sensor</td>
</tr>
</tbody>
</table>

* bar=0…250, (350°C). ** ±10V

Table III: Technical Data (Sensor)

<p>| | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Measuring range</td>
<td>bar</td>
<td>0…250</td>
</tr>
<tr>
<td>Calibrate ranges</td>
<td>bar</td>
<td>0…50, 0…100, 0…150, 0…250</td>
</tr>
<tr>
<td>Overload</td>
<td>bar</td>
<td>300</td>
</tr>
<tr>
<td>Sensitivity</td>
<td>pC/bar</td>
<td>≈ -20</td>
</tr>
<tr>
<td>Natural frequency, nominal</td>
<td>kHz</td>
<td>≈ 160</td>
</tr>
<tr>
<td>Linearity in all ranges (at 23°C)</td>
<td>%/FSO</td>
<td>≤± 0,4</td>
</tr>
<tr>
<td>Acceleration sensitivity</td>
<td>bar/g</td>
<td>&lt;0,0005</td>
</tr>
<tr>
<td>Operating temperature range</td>
<td>°C</td>
<td>-20…350</td>
</tr>
<tr>
<td>---------------------------------------------</td>
<td>----</td>
<td>---------</td>
</tr>
<tr>
<td>temperature min./max.</td>
<td></td>
<td>-50…400</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sensitivity</th>
<th>%</th>
<th>≤± 0,5</th>
</tr>
</thead>
<tbody>
<tr>
<td>200±50 °C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23…350 °C</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Short term drift (thermal shock)</th>
<th>bar</th>
<th>≤± 0,5</th>
</tr>
</thead>
<tbody>
<tr>
<td>(at 1 500 l/min, pmi = 9 bar)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δp (Short therm drift)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Δp_{mi}</td>
<td>%</td>
<td>≤± 2</td>
</tr>
<tr>
<td>Δp_{max}</td>
<td>%</td>
<td>≤± 1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Insulation resistant at 23 °C</th>
<th>Ω</th>
<th>≥ 10^13</th>
</tr>
</thead>
<tbody>
<tr>
<td>Shock resistance</td>
<td>g</td>
<td>2 000</td>
</tr>
<tr>
<td>Tightening torque</td>
<td>N·m</td>
<td>1,5</td>
</tr>
<tr>
<td>Capacitance, without cable</td>
<td>pF</td>
<td>5</td>
</tr>
<tr>
<td>Weight with cable</td>
<td>g</td>
<td>30</td>
</tr>
<tr>
<td>Connector, ceramic insulator</td>
<td>-</td>
<td>M3x0,35</td>
</tr>
</tbody>
</table>

**Table IV: Technical Data (Amplifier)**

<table>
<thead>
<tr>
<th>Frequency response: Standard filter</th>
<th>Hz</th>
<th>180, 000</th>
</tr>
</thead>
<tbody>
<tr>
<td>Accuracy</td>
<td>%</td>
<td>≤±0.50</td>
</tr>
<tr>
<td>Time Constant (range dependent):</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Long</td>
<td>s</td>
<td>0…100000</td>
</tr>
<tr>
<td><strong>Time Constant Resistor:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-----------------------------</td>
<td>-----------------------------</td>
<td></td>
</tr>
<tr>
<td><strong>Long</strong></td>
<td>Ω</td>
<td>&gt;114</td>
</tr>
<tr>
<td><strong>Medium</strong></td>
<td>Ω</td>
<td>111</td>
</tr>
<tr>
<td><strong>Short</strong></td>
<td>Ω</td>
<td>19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th><strong>Noise:</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>referred to with input shield</td>
<td>pCrms</td>
</tr>
<tr>
<td>1 pC/V max</td>
<td>μVrms</td>
</tr>
<tr>
<td>100 pC/V max</td>
<td>300</td>
</tr>
<tr>
<td>100000 pC/V max</td>
<td>200</td>
</tr>
</tbody>
</table>

| **Drift MOSFET leakage current** | pC/s | ≤± 0.03 |
| **Zero Offset in Reset typical** | mV | 0.5 |

<table>
<thead>
<tr>
<th><strong>Output:</strong></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Connector</strong></td>
<td>BNC neg., gnd. Isolated</td>
</tr>
<tr>
<td><strong>Impedance</strong></td>
<td>Ω</td>
</tr>
<tr>
<td><strong>Voltage Range</strong></td>
<td>V</td>
</tr>
<tr>
<td><strong>Current Limit</strong></td>
<td>mA</td>
</tr>
<tr>
<td><strong>Display</strong></td>
<td>type</td>
</tr>
<tr>
<td><strong>Serial Interface (RS-232C)</strong></td>
<td></td>
</tr>
<tr>
<td><strong>Connector</strong></td>
<td>9 pin D-Sub.</td>
</tr>
<tr>
<td>Baud Rates</td>
<td>150…9600</td>
</tr>
<tr>
<td>------------------</td>
<td>----------</td>
</tr>
<tr>
<td>Maximum Cable Length</td>
<td>m/ft</td>
</tr>
<tr>
<td>Remote Control Connector</td>
<td>DIN 45322</td>
</tr>
<tr>
<td>Temperature Range Operating</td>
<td>oF</td>
</tr>
<tr>
<td>Temperature range storage</td>
<td>oF</td>
</tr>
<tr>
<td>Humidity Non-condensing</td>
<td>%</td>
</tr>
<tr>
<td>Power Line:</td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>VAC</td>
</tr>
<tr>
<td>Frequency</td>
<td>Hz</td>
</tr>
<tr>
<td>Power Consumption max.</td>
<td>VA</td>
</tr>
</tbody>
</table>

**Fuel Line Pressure Sensor.**

Another parameter that needs to be measured is the pressure inside the fuel lines because as different fuels are introduced, different viscosities follow suit and change pressure in the fuel lines. This results in a change in injection, that affects many engine characteristics. The pressure sensor chosen for this task was another pressure sensor from Kistler specifically designed for this application. However, this pressure sensor is not piezoelectric, it is strain gauge based and still needs an amplifier and a power source.

The sensor was attached to a clamp that wraps around the fuel line, and the sensor was placed directly above a hole drilled in the fuel line. (Figure ) This allowed for the sensor to read the pressure inside the lines, and the clamp seals around the hole to keep
the pressure and the fuel contained. The shematic of the fuel line pressure sensor is similar to that of the pressure probe setup in Figure 30. The output of the amplifier was 0-10 volts, and the pressure range was from 0-1000 bar; therefore giving a 100 bar/volt conversion factor. (Figure 32)

Figure 31 DWG of Fuel Line Pressure Sensor Setup
High Speed Data Acquisition System

All of the previous instruments (encoder, pressure probe, fuel line pressure sensor) have voltage outputs and were collected by a DAQ system. For DAQs the reading was dependent on a sampling rate in the units of hertz (Hz), this was a given number of cycles per second. If a DAQ was set for 1MHz, it would collect one million data points per second. However, when using a DAQ in engine research, data it was necessary to collect data dependent on physical positions of the engine rotation. If data collection was time based, that origin of time can begin anywhere in the engine cycles and the piston can be anywhere in its cycle and there was no accurate way to determine where the engine was in its cycle. The rotary encoder enabled crank angle dependent data collection.

The rotary encoder is aligned with TDC of the index pulse, when the engine is at TDC the index pulse occurs. The encoder has two other channels that have 2000 pulses/rev; one full revolution results in a pulse every 0.18 degrees. Given the number of
pulses generated by one revolution of the slotted disk (resolution), the angular position of
the encoder can be determined.

In order to collect the analog signal, the acquiring signal would have to be 20
times the frequency of the incoming signal. The rotary was mounted to an engine
rotating at maximum 3000 rpm’s which produces 50 revs/sec, and each rev produces
2000 pulses from the encoder. This leads to 100,000 pulses per second and required an
acquiring signal rate of 2MHz; this is the maximum sampling frequency necessary for
acceptable data collection.

**Yokogawa Oscilloscope.**

A third method of DAQ systems was to use a high speed DAQ oscilloscope. The
Yokogawa DL750 oscilloscope was used as a DAQ device which is enabled to have a
sampling rate of up to 10MHz; this exceeds the needs in this study.

With the USB ports accessible by a thumb drive, data can be collected by starting
the acquisition, stopping the acquisition and then selecting a file for that data sample to
be saved. Also, once the file name is written and chosen, an option is available to where
the file name is kept the same, but is changed slightly by varying one number on the file
name; example: COMBXXXX. Therefore, while any experiment is running at a given
condition, data can be collected and stored several times during that condition. This
allows for comparing multiple sets of data for statistics, repeatability, and consistency;
and all of this is built in to the oscilloscope without having to write any codes.

**Sampling Frequency.**

The previous rule of sample frequency, twenty times the frequency of the original
signal, was applied to the oscilloscope. To test this setup, various sampling rates were set
on the oscilloscope, encoder rotating at 3000 rpm, and then data was collected from the encoder to show the results of this sampling rate. 2MHz demonstrated the best results for DAQ. (Figure 33) This was a time based DAQ setup.

![Encoder Channels Collected at 2MHz](image)

Figure 33 Example of Encoder Signal Collection

**External Clock Setting.**

Based on the same idea used in the LabView, using the 2000 pulses/rev channel as a trigger, can collect data with a corresponding crank angle. The three signals collected by the DAQ was the index pulse, glow plug pressure sensor, and fuel line pressure. (Error! Reference source not found.) Using channel B as an external clock, the number of data points collected were 0.18° apart. Each collection of data was a minimum of 4000 data points; 1 engine cycle = 720°, which equals 2 revolutions and at 2000 pulses/rev, this leads to 4000 data points. But more than one cycle was collected, therefore the sampling length was set to 25,000 data points; giving at least 6 full cycles.
NOx Emissions Equipment

During the research of this study, the emissions of main concern were that of nitrogen oxide type (NOx). This consists of both nitrogen monoxide (NO) and nitrogen di-oxide (NO₂) which both are referred to as NOx. An exhaust emissions analyzer for NOx is necessary for the completion of this study and needs to reach within the range of emissions that will be produced by the engine being used.

The NOx analyzer chosen was made by Horiba. (Figure 34) This analyzer uses an oxygen type sensor that screws into the exhaust of the engine exhaust manifold and is made of Zirconia which enables it to determine the amount of NOx in the exhaust. Zirconia is a conductive ceramic that conducts electricity very well. The sensor is heated up by the Horiba analyzer module that provides power and takes and displays the readings of the NOx levels in parts per million (ppm). The readings are based upon the amount of oxygen that passes through the sensor which causes the electrodes connected to the zirconia material to excite a voltage to the analyzer.

Figure 34 Horiba NOx Analyzer (Horiba Automotive Test Systems)
For the sensor being used, it needs to be calibrated for accurate readings, but with this setup the sensor comes with a certificate of calibration. (Figure 35) The only thing that needed to be done was to test the sensor by turning the sensor on and swinging it slightly in the air and measure the amount of oxygen in the air and then compare that value with that day’s oxygen level reading from the local weather station. This was completed after the appropriate setup settings were applied to the NOx analyzer module; the results of percent oxygen from the weather station and the oxygen measured were in compliance with one another.

<table>
<thead>
<tr>
<th>TEST DATA</th>
<th>CH No.</th>
<th>720</th>
<th>DATA</th>
</tr>
</thead>
<tbody>
<tr>
<td>CAL_points</td>
<td>00</td>
<td>00</td>
<td>4</td>
</tr>
<tr>
<td>Z</td>
<td>07</td>
<td>07</td>
<td>575</td>
</tr>
<tr>
<td>A</td>
<td>08</td>
<td>08</td>
<td>2.410</td>
</tr>
<tr>
<td>B</td>
<td>09</td>
<td>09</td>
<td>0.1838</td>
</tr>
<tr>
<td>NOzero</td>
<td>11</td>
<td>11</td>
<td>0ppm</td>
</tr>
<tr>
<td>NOmid</td>
<td>12</td>
<td>12</td>
<td>922ppm</td>
</tr>
<tr>
<td>NOspan</td>
<td>13</td>
<td>13</td>
<td>1828ppm</td>
</tr>
<tr>
<td>Noahigh</td>
<td>14</td>
<td>14</td>
<td>2920ppm</td>
</tr>
<tr>
<td>Ip2zero</td>
<td>21</td>
<td>21</td>
<td>0.213</td>
</tr>
<tr>
<td>Ip2mid</td>
<td>22</td>
<td>22</td>
<td>3.587</td>
</tr>
<tr>
<td>Ip2span</td>
<td>23</td>
<td>23</td>
<td>6.721</td>
</tr>
<tr>
<td>Ip2high</td>
<td>24</td>
<td>24</td>
<td>10.391</td>
</tr>
<tr>
<td>CAL_points</td>
<td>10</td>
<td>10</td>
<td>3</td>
</tr>
<tr>
<td>O2Mspan</td>
<td>15</td>
<td>15</td>
<td>−18.71%O2</td>
</tr>
<tr>
<td>O2zero</td>
<td>16</td>
<td>16</td>
<td>0.00%O2</td>
</tr>
<tr>
<td>O2span</td>
<td>17</td>
<td>17</td>
<td>20.6%O2</td>
</tr>
<tr>
<td>Ip0Mspan</td>
<td>25</td>
<td>25</td>
<td>−3.503</td>
</tr>
<tr>
<td>Ip0N2</td>
<td>26</td>
<td>26</td>
<td>−0.006</td>
</tr>
<tr>
<td>Ip0span</td>
<td>27</td>
<td>27</td>
<td>3.734</td>
</tr>
<tr>
<td>LIN</td>
<td>29</td>
<td>29</td>
<td>2</td>
</tr>
</tbody>
</table>
Summary

The setup of the study was discussed and explained in detail. Information and measurements from all of the above mentioned topics were used during engine testing. The engine initially ran on diesel fuel at 70 percent load at 2000 rpm during the warm up time; usually 15 minutes, until the dyno and engine oil was at appropriate temperatures. Following this, the fuel system was switched to the test fuel until diesel fuel was entirely replaced throughout the fuel system and the fuel lines on the engine. The engine speed was increased to desired speed and 100 percent load. The fuel system was switched to the test fuel in the burette and a timer used to measure the time of fuel consumption. During the fuel consumption timing, data was collected using the DAQ, LFE, NOx sensor, and thermocouples and recorded in a test sheet. The fuel consumption and data collection was repeated a total of five times for each fuel blend and engine speed.
Chapter 6

Discussion and Results

Introduction

These are used to discuss and explain the results from this study. Herein the results of all blends at N=2200 rpm and 4.78 bmepl (100% load) are presented and discussed.

Fuel Specifications

Technical grade methyl oleate with 73% purity was purchased from TCI America (Portland, OR). As previously stated, methyl oleate has been suggested in the past as a compound for enrichment in biodiesel fuels to improve biodiesel fuel properties. As seen from previous studies oleic acid is definitely a suitable fatty acid for enrichment in a fatty acid profile. The enrichment of vegetable oils using methyl oleate is typically performed with technical-grade level, 60–90% purity. The melting point of -20 °C would suffice for most cold climate environments; however, for extreme conditions, an even lower melting point would be desired. As reported the kinematic viscosity of methyl oleate increases from 4.50 mm²/s at 40 °C to 21.50 mm²/s at -10 °C, with the latter value being nearly the kinematic viscosity of some vegetable oils at 40 °C. The oxidation stability, of less than 3 hr (per Rancimat test at 110 °C), for methyl oleate does not meet either the ASTM or EN standards. Though the oxidative stability of methyl oleate is considerably greater than that of the polyunsaturated esters methyl linoleate and methyl linolenate, which still require an additive for these materials to meet the specifications in biodiesel standards.

The density of diesel no.2 and methyl oleate mixtures varies with the mass participation of the fatty acid into the mixture having values from 0.85 g/cm³ to 0.88 g/cm³ for
O100. The cetane number of methyl oleate exceeds the minimum biodiesel standards (51 in EN 14214 and 47 in ASTM D6751) as seen in Figure 1. The value of Cetane number for diesel in this study was 47 and that of O100 was 56 as presented in Table V.

The peanut FAME used during the combustion investigations was produced in the laboratory following the method described in the previous chapter. The properties of the peanut FAME are presented in Table V.

Table V: Properties of reference fuels

<table>
<thead>
<tr>
<th>Property</th>
<th>Diesel No.2</th>
<th>Methyl Oleate</th>
<th>Peanut FAME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Number</td>
<td>40-55</td>
<td>56</td>
<td>54</td>
</tr>
<tr>
<td>Density</td>
<td>0.85 g/cm³</td>
<td>0.88 g/cm³</td>
<td>0.87 g/cm³</td>
</tr>
<tr>
<td>Viscosity @40°C</td>
<td>1.9 - 4.1 mm²/s</td>
<td>4.51 mm²/s</td>
<td>4.9 mm²/s</td>
</tr>
<tr>
<td>LHV</td>
<td>42.6 MJ/kg</td>
<td>39.93 MJ/kg</td>
<td>34,[14]</td>
</tr>
<tr>
<td>MW</td>
<td>233 g (EPA)</td>
<td>296.5 g</td>
<td>~292 g</td>
</tr>
<tr>
<td>Saturation Degree</td>
<td>NA</td>
<td>saturated</td>
<td>93</td>
</tr>
<tr>
<td>Flash Pt.</td>
<td>100°C min</td>
<td>163°C</td>
<td>176 °C</td>
</tr>
<tr>
<td>Cloud Pt.</td>
<td>-16.1°C</td>
<td>-12.8°C</td>
<td>17 °C</td>
</tr>
</tbody>
</table>

**Dynamic Viscosity and Shear Stress of Test Fuels**

Viscosity is one of the most important properties of biodiesel because of its pronounced effect based on the operation of the fuel injection equipment, in particular at low temperatures where the increase in viscosity can lead to poor spray due to injector
clogging and inadequate fuel atomization. Poor atomization leads to increased carbon deposits causing increased wear to develop which in turn leads to decreased performance, with respect to mechanical efficiency and power output. However the higher viscosity range of biodiesel has been seen to help to reduce barrel/plunger leakage and increase injector efficiency in the engine.

The dynamic viscosity of fatty acid methyl esters is highly influenced by the structure of the compounds. Influencing factors are chain length, double bond position, number of double bonds, and nature of double bonds. Usually, the hydrocarbons in petroleum diesel exhibit lower viscosity that directly affect the fuel spray atomization and ultimately, the formation of carbon deposits in the engine.

Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. Also, factors such as double bond configuration influence viscosity (a cis double bond configuration giving a lower viscosity than a trans configuration) while double bond position effects viscosity to lesser extent. Branching in the methyl ester, however, has little or no influence on viscosity, again showing that this is a technically promising approach for improving low-temperature properties without significantly affecting other fuel properties.

The dynamic viscosity of fatty compounds is considerably influenced by the structure of the compound. Influencing factors are chain length, double bond position, number of double bonds, and nature of double bonds. Usually, the hydrocarbons in petroleum diesel exhibit lower viscosity that would affect the fuel spray atomization and ultimately, the formation of carbon deposits in the engine. The viscosity is one of the
most important properties of biodiesel because of its pronounced affect based on the operation of the fuel injection equipment, in particular at low temperatures where the increase in viscosity can lead to poor spray due to injector clogging and inadequate fuel atomization. Poor atomization leads to increased carbon deposits causing increased wear to develop which effects performance, with respect to mechanical efficiency and power output. However the higher viscosity range of biodiesel has been seen to help to reduce barrel/plunger leakage and increase injector efficiency in the engine. According to Knothe and Steidltty the viscosity of biodiesel is slightly higher than that of diesel, but of less magnitude than the original vegetable oil of fat. Generally the aliphatic and aromatic hydrocarbons, which are the major components of petroleum diesel, display a smaller viscosity range with lower viscosities due to their lack of oxygen. The length of the chain with the same number of carbon atoms and the difference in increasing the viscosity hydrocarbons are smaller for the esters of the fatty acids. For the same number of carbon atoms, composed of fatty acids are more viscous. Double bonds reduce kinematic viscosity in fatty compounds and aliphatic hydrocarbons. The viscosity-lowering effect is greater in the fatty compounds, which may be a result of the double bond position. However, varying the double bond position towards the middle of the chain has comparatively little effect on viscosity, so that double bond within the region should not be of significance for biodiesel.

Viscosity increases with chain length (number of carbon atoms) and with increasing degree of saturation. This holds also for the alcohol moiety as the viscosity of ethyl esters is slightly higher than that of methyl esters. Factors such as double bond
configuration influence viscosity (cis double bond configuration giving a lower viscosity than trans) while double bond position effects viscosity less. Branching in the ester moiety, however, has little or no influence on viscosity, again showing that this is a technically promising approach for improving low-temperature properties without significantly affecting other fuel properties. Values for dynamic viscosity and kinematic viscosity of neat fatty acid alkyl esters are included in Table 2.

For all the fuel mixtures developed in the viscosity studies (0-100% Methyl Oleate and 0-100% peanut FAME), the viscosity was investigated at various temperatures to determine changes in shear stress with a Brookfield Viscometer DV II Pro type. Fitted with the Small Sample Adapter attachment the instrument selection came from the conditions that the viscometer had to operate from 0-60 °C, handle low viscosity liquids, ease of maintenance, and resistant to contamination. The results showed that viscosity increases in proportion with the percentage weight of the methyl oleate to petroleum diesel used to produce the fuel samples. The viscosities and shear stress of the samples were measured at temperatures between 25°C and 60°C as seen in Figures 36, 37, 38, and 39.

For the diesel engines, the fuels’ viscosity is essential since it has influence on the droplet size, penetration, and mixing rate with the air, vaporization, emissions, smoke, and wall deposits. As a result, engine efficiency and emissions characteristics are determined. The diesel engines require a fuel viscosity between 1-20 cSt with a maximum for very large bore engines of about 100 cSt. The viscosity study of the test fuels, took place at various viscometer spindle speeds ranging from 1.5-100 rpm and
25°-60°C, verifying that the viscosity of the test fuels and diesel blends are slightly higher than that of diesel alone, and ranged from 2-7 cP depending on the biodiesel content.

These results determined that the test fuels were within the ASTM viscosity standard when using up to a 50% diesel-biofuel blend.

Figure 36 Dynamic viscosity comparison of methyl oleate blended with petro diesel
Figure 37 Dynamic viscosity comparison of peanut FAME blended with petro diesel
Figure 38 Shear stress comparison of methyl oleate blended with petro diesel
Figure 39 Shear stress comparison of peanut FAME blended with petro diesel
Energy Content of Test Fuels

The heat of combustion for the tested fuels has been investigated using a constant volume calorimeter. The temperature data was recorded using a data collector and temperature probe. It is seen in Fig. 2 that the lower heating value (LHV) calculated from fuel testing increases in difference from the reference LHV as the percentage of peanut FAME in the blend increases. The difference between the LHV of P100 to diesel No. 2 is 17% for the experimental values compared to 20% for the reference values [14]. The error in the experimental values is believed to originate from impurities such as excess methanol, residual catalyst, and soap.

![Lower heating value comparison of peanut FAME blends](image)

*Figure 40 Lower heating value comparison of peanut FAME blends*
Cloud Point Evaluation of Peanut FAME

The fuel property most important to low temperature operation of diesel engines is the cloud point, that for biodiesel is typically higher than diesel No. 2. The cloud point is the temperature at which a cloud of wax crystals first appears in a liquid upon cooling and is an indicator of the lowest operation temperature of a fuel. Operating temperatures below the cloud point for diesel fuel can result in fuel filter clogging due to the wax
crystal formation. The cloud point is determined by visually inspecting for a haze in normally clear fuel, while the fuel is cooled under carefully controlled conditions.

In Figure 42, it is seen that P100 had a relatively high cloud point of 18°C. When the sample of peanut FAME was placed in the rock salt and ice bath, the sample almost immediately turned cloudy and was completely frozen at 8°C. As the peanut FAME was blended with diesel No. 2 it can be seen that the cloud point steadily decreases. A P20 blend (20% peanut FAME 80% diesel No. 2) was able to reach a temperature just below 0°C. The high cloud point temperature of peanut FAME is related to the methyl stearate and palmitate composition of peanut oil, which are solid at room temperature. The peanut oil contains approximately 20% stearic and palmitic fatty acids, which are saturated esters with no double bonds leading to increased density.
Figure 42 Cloud point of peanut FAME blended with petro diesel
Thermal Analysis

The thermo gravimetric and differentiual thermal analysis were conducted to investigate the oxidation properties of the test fuels. The results demonstrated that up to about 150°C, the peanut FAME is stable with little vaporization occurring compared with diesel from which lighter fractions were already starting to release at 75°C, seen in Figures 43 and 44. The methyl oleate blends’ bulk vaporization is completed at approximately 350°C with a small amount of some heavier fractions still being released up to 600°C, compared with diesel that at 450°C is completely vaporized, seen in Figures 45 and 44 respectively. The region of endothermic reaction of the peanut FAME was considerably less than that of the diesel or oleic ester blends. The peanut FAME endothermic reaction takes place in the range from ambient to 250 °C, while the diesel and methyl oleate blends range is increased to about 400 °C. The exothermic reaction of the peanut FAME is considerably longer than either the diesel or methyl oleate blends. The largest fraction of peanut FAME is oxidized between 250 and 300°C, then there can be seen continued lesser reaction out to 450°C. This is attributed to the multiple components that comprise the peanut FAME, where as the diesel and methyl oleate blends are “pure” substances.
Figure 43 Thermal analysis of peanut FAME
Figure 44 Thermal analysis of petro diesel
Figure 45 Thermal analysis comparison of methyl oleate blends
Combustion Process for Compression Ignition Engines

In a CI engine, the combustion process is a complex process with multiple dependent phenomenons that affect the combustion process. In a CI engine air inducted during the intake stroke followed by fuel being injected about 13 CAD before the piston reaches TDC. The fuel is sometimes injected at high pressures to help atomize the fuel so that it may vaporize and mix well with the surrounding air. As the piston continues to approach TDC, pressure rises and the surrounding air temperature rises and the mixed air and fuel ignites, thus starting combustion and ending ignition delay. (Figure 46) The fuel is not introduced in one single shot, but is sprayed over several CAD of rotation, therefore the process of fuel injection, mixing, compressing, igniting, and burning is ongoing until all available fuel is burned or the engine has rotated through the cycle.

Figure 46 Example of combustion data from a compression ignition engine
Lambda vs Speed

Lambda (λ) is known as the stoichiometric air to fuel ratio during the combustion process. Lambda is only affected by the amount of fuel and/or the amount of air intruduced into the engine cycle. This ratio is of importance for engine performance, combustion and emissions.

The speed of a CI engine engine is controlled by the amount of fuel injected in to the combustion chamber during each cycle. More fuel introduced leads to more fuel being burned which leads to more energy being released and therefore accelerates the engine into greater speeds.

![Lambda vs. Load](image)

Figure 47 λ vs. Load Example

The λ that is normally measured is the overall A/F ratio of the combustion process. During the compression, moving into the combustion process, fuel is injected in the combustion chamber and air mixes with the fuel and combustion occurs. But throughout this multi phenomenon process in the engine cycle, not all of the fuel in the
system is undergoing combustion because fuel is being injected over a period of time while combustion is occurring, and there are many factors that affect the combustion process. As mentioned before, sometimes $\lambda$ is greater than 1 which means there is more air than fuel, but this is the overall chamber ratio because during the process of combustion, combustion only occurs when the fuel and air has reached stoichiometric ratio; there are other regions of the air/fuel mixtures that are not at stoichiometric ratios and are not undergoing combustion but are approaching ignitable conditions.

**NO$_X$ Emissions Formation**

There are three main processes for the formation of NO$_X$ emissions: Zeldovich mechanism or Thermal NO, Prompt NO formation by Fenimore, and Fuel NO. The Zeldovich process is when the temperature of the combustion causes oxygen molecules to break apart and then the nitrogen from the air bonds with the free oxygen molecules to form either NO or NO$_2$; NO contributes to over 90% of NO$_X$ formation. The Prompt NO formation is suggest that NO forms from cyanide (HCN) produced in combustion, and is then oxidized to form NO; this process is significant only in rich flames and is not heavily dependent on temperature like the Zeldovich mechanism. The third process is Fuel NO and is very low in contribution to NO$_X$ formation. This mechanism is the nitrogen in the fuel that is converted to NO. (Hsu, 2002)

The most common and prominent NO$_X$ forming process is the Zeldovich process, which is why the trend of NO$_X$ emissions is to increase as the temperature of combustion increases, and combustion temperature occurs under heavy loads and high speeds. A lot of studies have been completed in the past and have shown that the general production of NO$_X$ is as follows:
O+N₂ = NO + N
N + O₂ = NO + O
N + OH = NO + H

NOx forms greatly at the beginning of the combustion process in the IDI engine because of such great initial temperature spike, later discussed, but NOx formation lowers towards the end of the cycle because of expansion of the chamber and a drop in temperature. It is also worth noting that NO is very stable at high temperature, but it oxidizes very rapidly into NO₂ when it reaches room temperature; this is sometimes why the emissions are referred to as NOx because the NO exits the engine into relatively colder temperatures and forms NO₂.

Zeldovich mechanism is the main formation process that is focused on here and is a strong function of temperature and makes it simple for assuming the amount of NOx formed just from the maximum bulk gas temperature. Therefore, the greater the bulk gas temperature, the more NO is formed.

Another theory is that during compression, some gas has burned and NOx is formed, but because of increasing pressures during compression, the temperature of these burned gases are heated up even more and produce more NO emissions; this is why a short ignition delay will help with reducing of NO emissions. This is true for the IDI engine which is later discussed. However, the point at which these gases are formed in the combustion chamber, the smaller the pressure difference between that point in time and the final pressure, the lower the amount of NO emissions are formed.
Indirect Injection Engine

The idea behind an IDI engine is that the fuel and air need to be mixed very rapidly, and with DI CI engines, this is achieved by the high pressures of injection, when the IDI accomplishes air fuel mixture by a swirl chamber. This allows for lower pressure injections; because the swirl chamber has such turbulent flow for the air to mix with the fuel and doesn’t have to rely on the high pressure of injection to help with the mixing of the air and the fuel. This chamber is separated from the main combustion chamber, and fuel is injected into the separate chamber, and as the engine compresses, the air is forced into the separate chamber usually in a swirl form to mix rapidly with the fuel being injected. From here, combustion begins in the separate chamber and then is forced down into the main combustion chamber where the piston is pushed back down during the power stroke. While the burning mixture is being pushed into the main combustion chamber, it’s turbulent and rapid flow continues to mix with the remaining air and fuel which will be burned as a result of being mixed thoroughly and the existence of a previously established flame front. The compression ratio of the IDI engine is much higher than a DI engine, around 23, and this is necessary because IDI engines are not as efficient as DI when starting in the cold.

In the swirl chamber of an IDI engine there are a couple of observations that need to be made. One is that IDI engines do not have a great initial spike in heat release as do the regular DI engines. This has to do with the engine design. There are less number of nozzles to direct the spray, therefore the fuel is sprayed tangentially into the chamber and the fuel collects on the walls. But at this point, air is rapidly entering into the separate chamber and beginning to mix with the fuel and autoignition occurs. When
the burning begins, temperature greatly rises, therefore evaporating the fuel that is sitting on the walls of the chamber and then causes a great spike in the heat release. Also, the high compression ratio of IDI engines makes for shorter ignition delays and low initial burning rate. (Heywood, 1988)

**Combustion Investigations**

The indicated diagrams in presented in Figures 48 and 49 shows the baseline reference cycles compared with diesel No.2 and were taken for 147 bars injection pressure for petroleum diesel and peanut FAME blends at 100% continuous load (4.78 bmep) and 2200 rpm. After the reference diagrams were obtained the load was maintained at 100% and the fuel was changed from 100% diesel to the test fuel without stopping the engine.

Based on the recorded pressures it can be concluded that the change in the amount of test fuel introduced into the system has a minimal effect on the average maximum combustion pressure, with the maximum combustion pressure remaining relatively constant for all fuel blends, The top combustion pressure at 2200 rpm and 100% load (4.78 bmep) for D100 was 69 bars. There was also noticed an offset of approximately 1 crank angle degree (CAD) later when comparing the 100% diesel to the test fuels.

The fuel’s bulk modulus, density, and viscosity can vary the needle lift and injection law in a hydraulic plunger-barrel injection system. A higher bulk modulus can cause a steeper rise in fuel pressure at the start of injection and the injector needle to open sooner. The experimental results for the fuel line pressures, presented in Figures 48 and 49, do not display any symptoms of the fuel line injector opening prematurely. The
mechanical injection system associated with this experiment using peanut FAME with 147 bar injection pressure displayed no modification in injection timing throughout the investigation. The engine was able to run relatively smooth and stable using the peanut FAME-diesel blend with no ignition difficulties observed.

Figure 48 Cylinder and fuel line pressure comparison of peanut FAME blended with petro diesel at 2200 rpm, 4.78 bmep
Apparent Heat Release

Using rapid data acquisition to record measurements of combustion chamber pressures every 0.18 degrees (0.01ms), it is possible to calculate the work performed within the cylinder with a high degree of certainty, the rate of change in internal energy of the combustible gases, and the heat transferred through the cylinder walls, as well as the instantaneous totals of these properties.

Figure 49 Cylinder and fuel line pressure comparison of methyl oleate blended with petro diesel at 2200 rpm, 4.78 bmep
Using the principals of the first law of thermodynamics and ideal gas law in combination with equivalent substitutions and the energy of a closed system, the rate of heat release is determined by the equation:

\[
\frac{dQ}{d\theta} = \frac{1}{\kappa - 1} V \frac{dP}{d\theta} + \frac{\gamma}{\gamma - 1} P \frac{dV}{d\theta}
\] (1)

The resulting apparent heat releases are shown in Figures 50-54. The apparent heat release represents the total heat lost through convection and radiation during the combustion cycle. From the results, it seems that the heat loss trend throughout the cycle is slightly higher for the 50\% blends compared to the D100.

Following the curves there is seen a negative heat release, from 330 to 355 CAD, representative of heat absorption and vaporization event that takes place when the fuel is injected. After that, there is seen a sharp rise, characteristic of the heat release during the premixed phase of combustion.

For all tested fuels this phase is exactly the same, with the main difference occurring between 365 to 385 CAD where the large concentration peanut FAME begins to form three separate peaks, which can be attributed to the heavy fractions of methyl esters that comprise the majority of peanut FAME, (palmitic, stearic, and oleic).

The oleic methyl ester-diesel blends had a slightly higher viscosity but in spite of the only 147 bars injection pressure used in the experiments, the injector provided good spray atomization, (in a single fuel injection event) and the engine could reach the target load with the original injection timing of 15 deg. BTDC, Figure 51. The engine ran
smooth and stable at 2200 rpm, 100% load, 4.78 bar bmep, with oleic methyl ester-diesel blend fuel. No ignition difficulties were observed and no pilot injection was needed.

The influence of component fatty acid properties, on injection timing and injection law compared with diesel fuel. Differences in bulk moduli between fuels are believed to result from differences in structure and intermolecular forces that dictate the free space between molecules. Aromatic compounds were found to be less compressible than their saturated counterparts, while long-chain paraffins are the most compressible hydrocarbons.

In addition to hydrocarbon structure, the presence of oxygen also influences biodiesel fuel’s compressibility. It creates a permanent dipole moment that causes oxygenated molecules to exhibit stronger hydrogen bonding and increased molecular affinity, compared to pure hydrocarbon molecules. These factors reduce the free space between molecules in biodiesel, decreasing its compressibility (high bulk modulus) relative to diesel fuel. The injection timing modification has been investigated experimentally and the interest comes from its influence on ignition delay and combustion.

The fuel’s bulk modulus, density, and viscosity can modify the needle lift and injection law in a hydraulic plunger-barrel injection system. Higher bulk modulus may cause a steeper rise in fuel pressure at the start of injection and the injector needle to open sooner. The experimental results presented in Figure 50 and 51 have shown that in the case of peanut FAME or methyl oleate, this hypothesis does not hold for the mechanical
injection system (plunger-barrel) with 147 bar injection pressure, and therefore no modification in injection timing has been visible throughout the experiments.

Figure 50 Heat release of peanut FAME blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 51 Heat release of methyl oleate blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 52 Heat release comparison of 20% peanut FAME
Figure 53 Heat release comparison of 20% methyl oleate
Mass Burnt and Ignition Delay

Due to higher viscosity, the biodiesel has a poorer atomization than petroleum diesel, which increases ignition delay. Allen (1999) stated that the Sauter mean diameter of methyl ester biodiesel is from 5-40% higher than petroleum diesel fuel’s. To determine the ignition delay, the apparent heat release was integrated from the start of injection to the end of the heat release. The start of injection was defined as the moment the fuel line reached 147 bar, at which fuel is injected, and the end of the heat release being the point the apparent heat release reaches zero. The ignition delay was defined as the duration from the crank angle at which the start of injection occurred to the crank angle at which 10% of the total mass was burnt. The higher viscosity of the peanut FAME has poorer atomization than petroleum diesel, which creates larger droplets and should increase ignition delay. Allen (1999) stated that the Sauter mean diameter (SMD) of methyl ester biodiesel is from 5-40% larger than petroleum diesel fuel. Another contributing factor to the ignition delays is the chemical effect, where higher Cetane numbers produce shorter ignition delays.

The engine investigated in this study presented an increased ignition delay for the peanut FAME blend, although negligible and could be accounted for measurements errors within the standards for the devices used, as seen in Figures 54 and 55. The apparent trend was the opposite for the methyl oleate blends but again were within the measurement errors associated with the devices used, seen in Figures 56 and 57.
Figure 54 Mass burnt comparison of peanut FAME blended with petro diesel
Figure 55 Ignition delay comparison of peanut FAME blends at 2000, 2200, and 2400 rpm
Figure 56 Mass burnt comparison of methyl oleate blended with petro diesel
Figure 57 Ignition delay comparison of methyl oleate blends at 2000 and 2200 rpm
**Instantaneous Volume Averaged Gas Temperature**

The heat transfer during combustion being quite complex due to the turbulent flows within the combustion chamber, will result in differences between the bulk gas and cylinder wall. The instantaneous volume-averaged gas combustion temperatures for the tested fuels throughout the cycle (calculated from the experimental pressure records) is presented in Figures 58-61. The maximum temperatures were nearly identical in all cases except when comparing the speeds. This trend was noticed throughout the calculations and across different test fuels, so was believed to be function of the engine used.

The exhaust temperature was confirmed by direct measurement in the exhaust valve port and used for the theoretical model calibration. The results showed an average exhaust gas temperature of about 340 deg. C for diesel and 335 deg. C for O20-O50.
Figure 58 Maximum in-cylinder temperature comparison of peanut FAME blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 59 Maximum in-cylinder temperature comparison of methyl oleate blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 60 Maximum in-cylinder temperature comparison of 20% peanut FAME blend at 2000, 2200, and 2400 rpm
Figure 61 Maximum in-cylinder temperature comparison of 20% methyl oleate blend at 2000, 2200, and 2400 rpm
Heat Fluxes During Combustion

In order to obtain the heat fluxes, the instantaneous volume-averaged in cylinder Reynolds number has been calculated as presented in equation 1 with the explanation of the terms in the Abbreviations section. The model can give accurate results and shows a very sharp difference between Re no. at TDC in expansion/intake stroke of about 10,000 versus 103,000 at TDC in combustion. The calculated Reynolds number showed practically the same values and trends for all fuels.

\[ R_e(\alpha) = \frac{\rho(\alpha)S \cdot n \cdot D}{30 \cdot \mu(\alpha)} \]  (eq.1)

Where the air viscosity is calculated with the following formula:

\[ \mu(\alpha) = 4.94 \cdot \frac{1273.15 + 110.4}{T_A(\alpha) + 110.4} \cdot \left(\frac{T_A(\alpha)}{1273.5}\right)^{1.5} \cdot 10^{-5} \]  (eq.2)

The heat flux for both fuels was obtained by Annand model, further developed by Soloiu and was calculated with the instantaneous volume averaged gas properties at every time step of 0.08 ms as presented in equation 3.

The calculated Reynolds number into the cylinder throughout the cycle exhibited high values at TDC in combustion, over 100,000, with similar trend and values for all fuels.
The heat flux for both fuels was obtained by Annand model [10-11] and was calculated with the instantaneous volume averaged gas properties at every as presented in equation 1.

\[
q(\alpha) = A \frac{\dot{\lambda}_A(\alpha)}{D} R_c^{0.7} (T_A(\alpha) - T_w) + \sigma \cdot \varepsilon (T_A^4(\alpha) - T_w^4) \quad \text{(eq.3)}
\]

while the convection heat transfer coefficient:

\[
\dot{\lambda}_A(\alpha) = -1.2775 \cdot 10^{-8} \cdot T_A^2(\alpha) + 7.6696 \cdot 10^{-5} \cdot T_A(\alpha) + 0.0044488 \quad \text{(eq.4)}
\]

The convection flux was 1.55 MW/m$^2$, while the maximum radiation heat flux was about 0.65 MW/m$^2$ for all fuels, Figures 62-65 and summing to a total of 2.05-2.1 MW/m$^2$. The convection flux has a maximum earlier in the cycle compared to the radiation flux and following the zone of maximum turbulence location, while the crank angle to which the maximum radiation flux has been obtained is maximum temperature dependent and the results fit well with the study of Borman and Nishiwaki.
Figure 62 Heat fluxes comparison of peanut FAME blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 63 Heat fluxes comparison of methyl oleate blended with petro diesel at 2200 rpm, 4.78 bmep
Figure 64 Heat fluxes comparison of 20% peanut FAME blend at 2000, 2200, 2400 rpm
Figure 65 Heat fluxes comparison of 20% methyl oleate blend at 2000, 2200, and 2400 rpm
Heat Losses During Combustion

Based on the heat fluxes, the heat loses throughout the cycle have been calculated and the results are presented in Figures 66-69. The area under inner line represents the apparent (net) heat release, the area between inner and middle line represents the heat lost through convection, and the area between the exterior line and middle line, represents the heat lost through radiation. From these results seems that the heat loss trend throughout the cycle is very similar for all fuels. It is visible that there is minimal heat loss during combustion before TDC with increased convection losses at TDC for all fuels and first part of power stroke while the radiation losses slightly increase and show higher values for all test fuels.
Figure 66 Heat losses comparison of peanut FAME blends at 2200 rpm, 4.78 bmep
Figure 67 Heat losses comparison of methyl oleate blends at 2200 rpm, 4.78 bmep
Figure 68 Heat losses comparison of 20% peanut FAME at 2000, 2200, and 2400 rpm
Figure 69 Heat losses comparison of 20% methyl oleate at 2000, 2200, and 2400 rpm
Engine Efficiency and Specific Fuel Consumption

The engine’s mechanical efficiency using peanut FAME-diesel blends display an area of maximum efficiency at 2000 rpm for diesel, P20 and P35 then decreases by 10% for P50, as seen in Figure 70. The area of maximum of efficiency is extended out to 2200 rpm for the P20 blend with slight decreases seen for D100 and P35.

The mechanical efficiency of the engine while operating with methyl oleate blends shows a more varied output, seen in Figure 71. The highest efficiency was noticed at 2000 rpm for O35 but quickly decreased as the speed of the engine increased. The lowest efficiency is also seen for the O35 but at 2400 rpm.

The overall efficiency of the engine display opposite trends when comparing the peanut FAME blends to the methyl oleate blends, seen in Figures 72 and 73. As the peanut FAME content increases the overall efficiency of the engine increases but as the speed of the engine increases the efficiency decreases. In the case of the methyl oleate the efficiency decreases with increasing methyl oleate content and decreases with increasing engine speed.

Seen in Figures 74 and 75, the BSFC increases with increasing peanut FAME and methyl oleate content. The fuel consumption increased by 5% for P50 and 10% for O50. This is promising as it demonstrates the compatibility of peanut FAME-diesel blends for use in compression ignition engines. This result also demonstrates that a compromise must be made when trying to reformulate biodiesel as one issue is solved but another arises from the use of the neat methyl esters.
Figure 70 Mechanical efficiency of peanut FAME blends at 2000, 2200, and 2400 rpm

Figure 71 Mechanical efficiency of methyl oleate blends at 2000, 2200, and 2400 rpm
Figure 72 Overall efficiency of peanut FAME blends at 2000, 2200, and 2400 rpm

Figure 73 Overall efficiency of methyl oleate blends at 2000, 2200, and 2400 rpm
Figure 74 Specific fuel consumption comparisons of peanut FAME blends at 2000, 2200, 2400 rpm

Figure 75 Specific fuel consumption comparisons of methyl oleate blends at 2000, 2200, 2400 rpm
NOx and Soot Emissions

Seen in Figures 76-79, there is a similar trend when comparing the NOx emissions but a very different trend when comparing the soot emissions. These results are hopeful as there is not displayed a drastic increase in NOx emissions as biodiesel content increases.

Figure 76 NOx emission comparison of peanut FAME blends at 2000, 2200, and 2400 rpm

Figure 77 NOx emission comparison of methyl oleate blends at 2000, 2200, and 2400 rpm
The largest increase in soot increases for the peanut FAME blends can be seen at 2400 rpm for P35 (30%). The great increase in soot emissions for methyl oleate blends is about 10% at 2000 rpm for O20.

**Figure 78** Soot emission comparison of peanut FAME blends at 2000, 2200, and 2400 rpm

**Figure 79** Soot emission comparison of methyl oleate blends at 2000, 2200, and 2400 rpm
Chapter 7

Conclusions

The authors investigated the injection and combustion of peanut FAME-diesel blends from 20% to 50% (wt./wt.) in an indirect injection compression ignition engine. The test fuels demonstrated no ignition difficulties in a small diesel engine with a high compression ratio. For optimal operation neither intake manifold heating, pilot injection, nor increase in swirl ratio were needed.

The dynamic viscosity of the test fuels increased with larger peanut FAME content in the fuel blends, but was still within the acceptable ASTM standards for biodiesel.

P100 has a higher cloud point than diesel but when blended with diesel would be suitable for lower temperature environments.

With the peanut FAME-diesel blends the engine could reach the target load with the original injection timing of 10 deg. BTDC, no ignition difficulties were observed, and no pilot injection was needed.

The engine investigated had the premixed and diffusion combustion phases combined and presented a decreased ignition delay as the peanut FAME content increased, related to the higher Cetane number and higher viscosity of peanut FAME.

The convection flux was nearly the same for both P50 and D100, the largest increase occurred from the radiation flux contribution.
The heat loss trend throughout the cycle increased slightly as the peanut FAME content increased, with negligible heat loss during combustion before TDC and increased losses at TDC for all fuels and first part of power stroke.

The mechanical efficiency decreased with an increase in peanut FAME content. Contributing factors to this phenomenon are increased mean indicated pressure, increased mechanical work absorbed by the injection pump, and the interaction of the chemical characteristics of peanut FAME combustion.

The peanut FAME-diesel blend investigations displayed similar combustion characteristics to those of 100% diesel No. 2 supporting its use in direct injection compression ignition engines to contribute to meeting the goals for biofuel usage. The authors investigated the formulation, injection and combustion of a methyl oleate alternative fuel, a mixture of 20%-50% with diesel by weight obtained with favorable combustion properties.

The dynamic viscosity of the methyl oleate was by 50-100% higher than for diesel at any temperature and shear stress and the fuel has shown a very good stability with this composition.

The study revealed that by injecting the fuel in the engine at 147 bars, the spray could develop, and vaporization necessary for complete combustion in a small bore engine could be achieved. The new alternative fuel had no ignition problems in a production engine with high compression ratio, and neither intake manifold heating, pilot injection, nor increase in swirl ratio were needed for a good operation.
The ignition delay for methyl oleate blends was slightly shorter than that of the reference the diesel fuel and the heat release showed a favorable development for a high speed diesel engine operation, with both premixed and diffusion combustion phases compounded.

The engine investigation proved that 20-50% Methyl Oleate by wt. in diesel can be burnt in a diesel engine with a residence time of about 5-5.5 ms from the start of injection resulting in combustion duration of 60-65 CA, and the engine’s continuous power could be reached.

The cycle’s maximum pressure increased from 73 bars to 75 bars employing the methyl oleate and the maximum cycle temperature increased from 2120 K for D100 to 2155 K for O50 mixture.

The heat flux in the engine cylinder has shown similar values for both fuels while the cylinder heat losses are at a minimum during combustion before TDC with increased convection losses at TDC for all fuels and first part of power stroke while the radiation losses slightly increase and show higher values for O50.

The engine’s mechanical efficiency with oleic FAME showed lower values than that in diesel combustion of 78% versus 86% at 4.78 bmep while the engine overall efficiency obtained with any blend including diesel was constant at 32%.

The study showed that the new biodiesel produced from methyl oleate proposed by the authors has favorable combustion properties and very similar to those of diesel no 2. The subsequent stage of research will be emissions investigations of O20-O50.
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