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**Combustion of Diesel Fuel Blended with Partially Oxidized Biodiesel in
a Direct Injection Compression Ignition Engine**

A Thesis in
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by
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ABSTRACT

Many past studies have been conducted to address concerns over emissions from biodiesel fueled compression-ignition engines. These have shown that apart from increased emissions of oxides of nitrogen (NO_x), biodiesel fueled engine emissions are equivalent or lower than for petroleum diesel fuel. An important property to consider for the future conversion to petroleum/bio diesel fuel blends is oxidative stability. Biodiesel has low oxidative stability leading to the formation of undesirable compounds and property changes many times faster than petroleum-based fuel when exposed to air. As a result it is necessary to investigate possible implications of having aged, or partially oxidized, biodiesel in future diesel fuel blends.

An air-cooled direct-injected naturally aspirated Yanmar diesel engine with a custom designed exhaust gas recirculation (EGR) loop was chosen as the platform for the follow-up study due to its flexibility and low fuel consumption. Fuels chosen for the follow-up study consisted of oxidized and non-oxidized versions of both canola and soy methyl esters blended into B20 fuel blends. These four fuels along with a baseline PC-10 pure petro-diesel were all run at 3600 RPM and 75% load at both 0% and 10% EGR settings. B20 is the most widely promoted biodiesel blend and is specifically called for in the Energy Policy Act (EPAAct) of 2005. The inclusion of EGR in the test protocol was because of the widespread use of EGR and a diesel particulate filter to achieve low emissions of both NO_x and particulates in production engines.

Blending partially oxidized biodiesel with petroleum diesel caused a decrease in total hydrocarbons (THC) and carbon monoxide (CO) emissions without a NO_x penalty, even when compared

with new biodiesel blends. There was however an overall penalty to NO_x emissions seen as an increase with all B20 blends, commonly called the biodiesel NO_x effect. As expected when EGR was added, all the fuels show a significant decrease in NO_x emissions while holding constant or increasing total particulate emissions. However when B20 based on partially oxidized biodiesel and 10% EGR are used together, very low total particulate and low NO_x are observed with both SME and CME.

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LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
AV	Acid Value
B20	20% Biodiesel, 80% Petroleum Diesel Fuel Blend
CI	Compression Ignition [Engine]
CME	Canola Methyl Ester
CN	Cetane Number
CO	Carbon Monoxide
DI	Direct Injection
DOC	Diesel Oxidation Catalyst
DPF	Diesel Particulate Filter
EGR	Exhaust Gas Recirculation
FAME	Fatty Acid Methyl Ester
GCMS	Gas Chromatography Mass Spectroscopy
IQT	Ignition Quality Test
LTC	Low Temperature Combustion
NO	Nitric Oxide
NO _x	Oxides of Nitrogen
Ox CME	Partially Oxidized Canola Methyl Ester
Ox SME	Partially Oxidized Soy Methyl Ester
PM	Particulate Matter
PV	Peroxide Value
SCR	Selective Catalytic Reduction
slpm	Standard Liter Per Minute
SME	Soy Methyl Ester
THC	Total Hydrocarbons
ULSD	Ultra-Low Sulfur Diesel

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Chapter 1

INTRODUCTION

1.1 Current and Future Biodiesel Use

Recent volatility in the price of petroleum based fuels has driven consumer interest in renewable fuels to an all-time high. Among renewable fuels available to consumers in the United States the two most prevalent are ethanol, in the form of various ethanol-gasoline blends, and biodiesel. The inherent efficiency gains of diesel compared to gasoline engines and production efficiency of biodiesel compared to ethanol make biodiesel the most attractive renewable fuel for the coming decades. Official estimates put the 2005 biodiesel production at 91 million gallons produced in the United States, roughly equivalent to 0.2% of the total diesel consumption [1]. Approximately half of the biodiesel produced during this time period was out of at least one ASTM specification for biodiesel fuel [2]. For this reason the biodiesel industry has placed increasing emphasis on fuel quality over increasing fuel output.

Future projections of biodiesel usage place it in the market as a blending agent rather than a neat fuel. Even using the most optimistic estimates of future technology, crop yields and production a maximum amount of approximately 7% of the current diesel use could be displaced with its bio-derived counterpart by the year 2030 [3]. Driving forces behind the development of additional biodiesel production in the market will be a combination of an increase in the cost of non-renewable petroleum fuels and tax incentives for renewable fuels. The start-up cost of producing more oil crops, setting up biodiesel processing plants, and distributing the fuel in biodiesel compatible systems will be a significant cost to attain levels equal to 7% biodiesel but should be somewhat offset by tax incentives of EPA. Overcoming these costs in addition to decreased oxidative stability of biodiesel are major concerns when incorporating a significant portion of biodiesel in the on-road fuel market.

1.2 Motivation

One of the properties of concern with biodiesel is its poor oxidative stability. When stored in non-airtight containers biodiesel lacking an anti-oxidant additive package quickly begins to degrade. The original methyl esters react with dissolved oxygen in the fuel and transform into peroxides. Peroxides in the fuel can go on to form other compounds such as volatile acids, complex organic molecules and polymers—causing many unwanted property changes such as increased water affinity and kinematic viscosity and decreased volumetric energy density. Consequences of these property changes are commonly increased droplet size within the fuel spray resulting in higher fuel consumption and increased particulate matter (PM) emissions because of the longer droplet life leading to less complete combustion and more time for pyrolysis respectively [4]. However, as mentioned above, the future of biodiesel is as a fuel blend stock and not as a neat (100% pure) form reducing the impact of fuel properties of the neat biodiesel fuel.

At maximum concentrations of 20% by volume any small changes in the physical properties of partially oxidized biodiesel are not enough to significantly alter those of the blended fuel, relative to B20 from fresh biodiesel. This means that when bio/petro diesel blends become more common on-road fuel, it is likely that aged biodiesel will be used with the final fuel remaining within ASTM specifications. Even if the physical properties are within specifications, partially oxidized biodiesel blends will have traces of chemical compounds that could significantly change the combustion characteristics of the fuel in a compression ignition engine. For instance, traces of biodiesel derived peroxides at amounts as small as 400 parts per million cause the fuel to be considered an explosive [5].

1.3 Compression Ignition Engines and Emissions

Compression ignition engines are extremely attractive power sources for future vehicles because of their peak efficiency of forty percent, compared to the thirty percent efficiency of spark ignited engines [6, 7]. Reasons why spark ignited engines dominate the automotive market in the United States are because of smoother and quieter operation of the engine and decreased tailpipe emissions. Engine-out emissions are similarly high between spark ignited and compression ignited engines but catalytic converters allow emissions mitigation from spark ignited engines. They utilize a three-way catalyst to oxidize THC and CO emissions to carbon dioxide and water while reducing NO_x emissions to nitrogen gas in an oxygen poor environment. There are not significant PM emissions from gasoline engines so all emissions other than carbon dioxide are almost completely eliminated from modern spark ignited engines.

Diesel engines have similar engine-out emissions to gasoline engines of CO, THC, and NO_x, but include significant PM emissions. The problem with diesel engines is that they usually have much higher concentrations of oxygen in their exhaust than spark ignited engines because they are designed to run at extremely lean overall stoichiometry. High concentrations of oxygen do not allow the three-way catalysts to work efficiently, therefore until 2007 all emissions that are usually neutralized in gasoline engines were emitted from the tailpipe of diesel engines with the addition of PM. As of 2007 diesel oxidation catalysts (DOCs) and diesel particulate filters (DPFs) became required equipment on all diesel vehicles sold in the United States due to stringent THC, CO, and PM emissions enacted that could not be met without the use of a DOC and DPF. Between 2007 and 2010 NO_x elimination systems such as urea selective catalytic reduction (SCR) systems must be incorporated into diesel vehicles to decrease NO_x emissions by 90% from the 2004 standard down to 0.20 g/hp-hr [8]. Unfortunately these systems are very complex and require frequent refills with urea, which is also a very reactive chemical that is hard to

handle and store. All of these modifications needed to make diesel engines have equivalent emissions to modern gasoline engines increase cost and decrease fuel efficiency and make it less advantageous to use a diesel engine in the United States.

An area of intense research with diesel engines is the use of advanced fuel chemistry and electronic injection strategies to eliminate particulate and NO_x emissions without the use of expensive and fuel wasting emission control systems. Among the first technologies used in diesel engines to control NO_x without the use of complex and expensive systems was an exhaust gas recirculation (EGR) system. The problem that vehicle researchers commonly run into with the use of EGR systems is the NO_x/particulate tradeoff. When EGR levels are increased, the lower combustion temperatures and oxygen concentrations in the cylinder decrease NO_x levels but allow more particulate to leave the engine without being oxidized. Conversely when EGR levels are decreased NO_x emissions increase and particulate emissions decrease [9]. Some low temperature combustion regimes controlled by advanced fuel injection strategies allow for simultaneous NO_x and particulate reduction, but these are generally limited to power outputs below levels usable for on-road vehicles. This leaves advanced fuel chemistry, such as the addition of oxygenates, that are meant to inhibit particulate matter formation while running with high levels of EGR to also inhibit NO_x formation. Therefore it is of interest to investigate the use of biodiesel and partially oxidized biodiesel as bio-derived oxygenates to decrease petroleum fuel use while efficiently decreasing particulate and NO_x emissions through use with EGR systems.

Chapter 2

LITERATURE REVIEW

2.1 Diesel Emission Controls

2.1.1 Turbocharging and Injection Pressure

Progression in high strength materials and sealing and electronic technologies have allowed for the use of ever-increasing injection and intake air pressure for diesel engines. These are both very important for reductions in PM and NO_x emissions while maintaining acceptable power output of diesel engines. Extremely high injection pressures of up to 1300 bar are commonly used on new diesel engines with correspondingly small ports on the injector to regulate the fuel flow. According to Martínez-Martínez increasing the injection pressure or the in-cylinder pressure prior to injection causes the fuel spray penetration to shorten [10]. Shortened fuel penetration indicates a higher degree of mixing in the cylinder leading to more uniform stoichiometry. Since soot is formed in locally fuel rich conditions a more uniform stoichiometry leads to a decrease in PM.

Turbocharging enhances mixing functions in the engine as mentioned above due to a higher density working fluid and also allows higher power to be developed from a given engine displacement. By allowing more power to be produced from a given engine displacement higher levels of EGR are able to be utilized for a given power output leading to the ability to lower brake-specific NO_x emissions [6].

2.1.2 Exhaust Gas Recirculation

One of the first techniques used to reduce diesel engine emissions was exhaust gas recirculation. Recirculating cooled exhaust increases the concentration of carbon dioxide and water and decreases the concentration of oxygen in the incoming air charge. Due to the high specific heat of both

carbon dioxide and water and the low concentration of oxygen, the peak combustion temperature in the cylinder remains much lower than without EGR. Since the Zeldovich reaction to form oxides of nitrogen are mostly thermally driven the lower combustion temperatures inhibit its formation with EGR. Unfortunately one of the side effects of lower combustion temperatures is increased particulate emissions [9, 11]. The reason for increased particulate emissions with lower combustion temperatures are because there is much more soot generated within the cylinder than is actually emitted from the engine. Most of the soot generated in the engine is oxidized before being expelled into the exhaust [12]. When the combustion temperatures and oxygen levels are suppressed by EGR it slows the oxidation process of the soot and allows more soot to escape in the exhaust. To try to get around the NO_x particulate tradeoff, there has been extensive research with after treatment systems, oxygenated fuels and low temperature combustion.

2.1.3 After Treatment

The simplest after treatment system that can be installed on a diesel engine is a diesel oxidation catalyst (DOC). Diesel oxidation catalysts use precious metal particles supported by ceramic similar to the three-way catalysts in spark ignited engines to oxidize THC and CO emissions to carbon dioxide and water. They are ineffective at oxidizing insoluble diesel PM emissions and cannot reduce NO_x emissions as three-way catalysts do for spark-ignited engines. To rid the exhaust of diesel particulate matter, a diesel particulate filter (DPF) is used to filter PM from the exhaust. Unfortunately DPFs rob the diesel engine of some of its efficiency by causing increased exhaust back pressure and requiring extra fuel to frequently regenerate by burning off of the accumulated PM. After a DOC and a DPF a third selective catalytic reduction (SCR) system is required to eliminate NO_x emissions and make compression-ignition engines as clean as spark-ignited engines. The addition of an SCR system adds complexity due to the need for liquid urea reactant to be introduced in the proper proportion in the exhaust system before the

catalyst. Other methods have been proposed and successfully used for NO_x reduction but urea SCR systems provide the best compromise between ease of implementation and effectiveness [13, 14].

2.1.4 Low Temperature Combustion (LTC)

Low temperature combustion is another method currently being researched as a way to get simultaneous NO_x and PM reductions without a need for exhaust aftertreatment. In order to enter an LTC regime, engines are started and warmed up using standard combustion modes. EGR is then added until PM emissions begin to decrease as EGR levels continue to rise, referred to as the LTC slope [15]. As the temperature in the cylinder falls from the high temperature combustion zone, the oxidation mechanisms for PM are first inhibited leading to an increase of PM as EGR increases. EGR levels of 50% or greater however, begin to inhibit pyrolysis of fuel rich zones of the fuel spray faster than soot oxidation mechanisms decrease: leading to an overall downward trend of PM emissions. At the same time as particulate matter decreases on the LTC slope, the extremely low combustion temperature leads to nearly non-existent NO_x emissions [16]. Unfortunately the use of LTC greatly limits the power output of an engine to nearly half of its original power output potential along with several other limitations making its current use for on-road diesel engines impractical.

2.1.5 Oxygenates

Oxygenates can help decrease emissions of THC, CO, and particulate emissions from diesel engines. Based on research conducted using six different diesel oxygenates it can be seen that regardless of the type of oxygenate there is a correlation to mass percent of oxygen in the fuel to the reduction of CO, THC and PM emissions compared to a standard diesel fuel [17]. Another study holds the type and concentration of the oxygenate constant (2-methoxy acetate at 15 and 20 percent by volume) while examining the effect of load and engine speed and use of oxygenate on engine out

emissions. When holding the load constant, the greatest overall reduction in THC, CO, and PM emissions is at low engine speed but there are reductions in these emissions at all engine speeds [18]. Oxygenates are proving to be extremely attractive routes to regulated emission control because all studies have not indicated a rise in NOx emissions as a result of the use of oxygenates.

2.2 Biodiesel

2.2.1 Biodiesel Characteristics

Physical and chemical differences of biodiesel from petroleum diesel are very important to understand for its future implementation as an oxygenate additive. In general biodiesel has higher kinematic viscosity, flashpoint and cetane number and lower volumetric energy density and oxidative stability compared to petroleum diesel. The best representation of a variety of biodiesel fuels can be found on table 2-1. Ramos et al. has a detailed chart of the properties for many different types of methyl esters commonly used for transportation fuel.

Table 2-1: Biodiesel Physical Characteristics [19]

Property	Units	Test method	Limits		Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
			Min.	Max.										
Ester content	wt.%	EN 14103	96.5		97.7	99.0	99.5	99.5	96.9	97.2	97.8	99.5	99.7	99.8
Kinematic viscosity, 40 °C	mm ² /s	EN ISO 3104	3.5	5.0	4.5	4.5	4.6	4.4	4.2	4.2	4.1	4.4	4.2	4.4
Flash point	°C	EN ISO 3679	120		176	178	176	170	171	177	175	174	172	170
Cetane number	-	- ^a	51		61	57	53	55	49	50	48	53	57	53
Oxidative stability, 110 °C	h	EN 14112	6.0		4.0	3.3	2.0	2.0	1.3	0.8	0.5	1.2	3.0	1.2
Acid value	mg KOH/g	EN 14104		0.50	0.12	0.13	0.10	0.16	0.14	0.15	0.27	0.21	0.17	0.15
Iodine value	g I ₂ /100 g	EN 14111		120 ^b	57	84	97	109	128	132	138	102	92	101
Linolenic acid content	wt.%	EN 14103		12.0	0.2	0.6	0.3	7.9	6.3	0.2	0.4	0.1	0.8	0.1
CFPP	°C	EN 116		- ^c	10	-6	17	-10	-5	-3	-6	-6	-6	-12
Methanol content	wt.%	EN 14110		0.20	0	0	0	0	0	0	0	0	0	0
Monoglycerides content	wt.%	EN 14105		0.80	0.17	0.67	0.32	0.41	0.21	0.37	0.28	0.31	0.27	0.40
Diglycerides content	wt.%	EN 14105		0.20	0.06	0.09	0.07	0.08	0.10	0.07	0.08	0.05	0.08	0.06
Triglycerides content	wt.%	EN 14105		0.20	0.04	0.03	0.03	0.03	0.07	0.04	0.03	0.06	0.02	0.03
Free glycerol	wt.%	EN 14105		0.02	0.01	0.00	0.01	0.01	0.07	0.00	0.00	0.00	0.00	0.00
Total glycerol	wt.%	EN 14105		0.25	0.06	0.19	0.11	0.09	0.00	0.11	0.09	0.13	0.07	0.09

The most important differences for combustion in a diesel engine between regular diesel and biodiesel are kinematic viscosity, cetane number and volumetric energy density. Cetane number (CN)

refers to the ignition quality of diesel fuels. Fuels with a higher CN have a shorter ignition delay, which is the time between injection into the engine and when the fuel ignites, resulting in better cold starting performance. A correlation has also been found between higher CN fuel and lower NO_x emissions as well as higher concentrations of peroxides have been shown to increase the CN of biodiesel [20]. Unfortunately the benefits of higher CN of biodiesel and oxidized biodiesel are offset by the emissions penalties from increased kinematic viscosity and decreased volumetric energy density compared to petroleum diesel. Increased viscosity leads to poorer fuel atomization by causing larger fuel droplets in the fuel spray resulting in higher PM emissions and worse cold starting ability. At the same time decreased volumetric energy density leads to a larger charge of fuel being injected under the same power demand from an engine and higher brake-specific fuel consumption [19, 21, 22].

2.2.2 Emissions from Biodiesel

Biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats, designated B100, and meeting the requirements of ASTM D 6751 [23]. Transesterification cleaves the bond between the fatty acids and the glycerol and usually substitutes a methyl group, forming three fatty acid methyl esters from the original triglyceride. Experimental results of the use of biodiesel and biodiesel blends in unmodified diesel engines have shown a consistent overall NO_x increase between 1 and 10%, depending on the concentration of biodiesel, unlike other oxygenate fuels [22, 24 - 27]. PM emissions commonly show a decrease of up to 40% [25 - 28]. One interesting observation to note is that the PM produced during neat biodiesel combustion is seen to be five times as reactive as the PM produced during petroleum diesel combustion [29]. Meanwhile emissions of total hydrocarbons (THC) and CO decreased as fuel oxygen levels increased [24, 25, 27]. However, in some isolated cases the PM, THC and CO emissions are observed to increase with an increasing level of biodiesel.

An extensive study of real-world diesel vehicles showed that THC and CO increased in some vehicles when using B20 fuel blends [30]. Particulate matter was observed to increase when biodiesel was blended with petroleum diesel and used in a naturally aspirated 2.2L Yue Loong diesel engine. Unfortunately solvent extraction was not carried out on the PM filters to determine how much of the PM was actually unburned fuel that condensed on the PM filter [31]. Since biodiesel is renewable and decreases all regulated emissions except NOx the best use for biodiesel in the future would be in a diesel engine with EGR.

2.3 Real World Biodiesel Use

2.3.1 Oxidative Stability of Biodiesel

Lower oxidative stability for biodiesel compared to standard diesel fuel has been well documented throughout literature. Table 2-1 shows no type of neat biodiesel can pass Rancimat testing according to ASTM D6751 or EN 14112 for fatty acid methyl ester (FAME) oxidative stability. The two main pathways paths for FAME degradation are a reaction with water and a reaction with oxygen to form carboxylic acids and peroxides respectively, shown in figure 2-1. Peroxides then go on to form volatile acids, polymers and complex organics, making the peroxide content more of an indication of the rate of oxidation than an indicator of the extent of oxidation [32, 33]. For a more accurate picture of the extent of oxidation the acid number can be measured using ASTM standard D-974-97. Acid number measurement gives a value of how many milligrams of potassium hydroxide are required to neutralize the carboxylic acid formed from the water-methyl ester reaction.

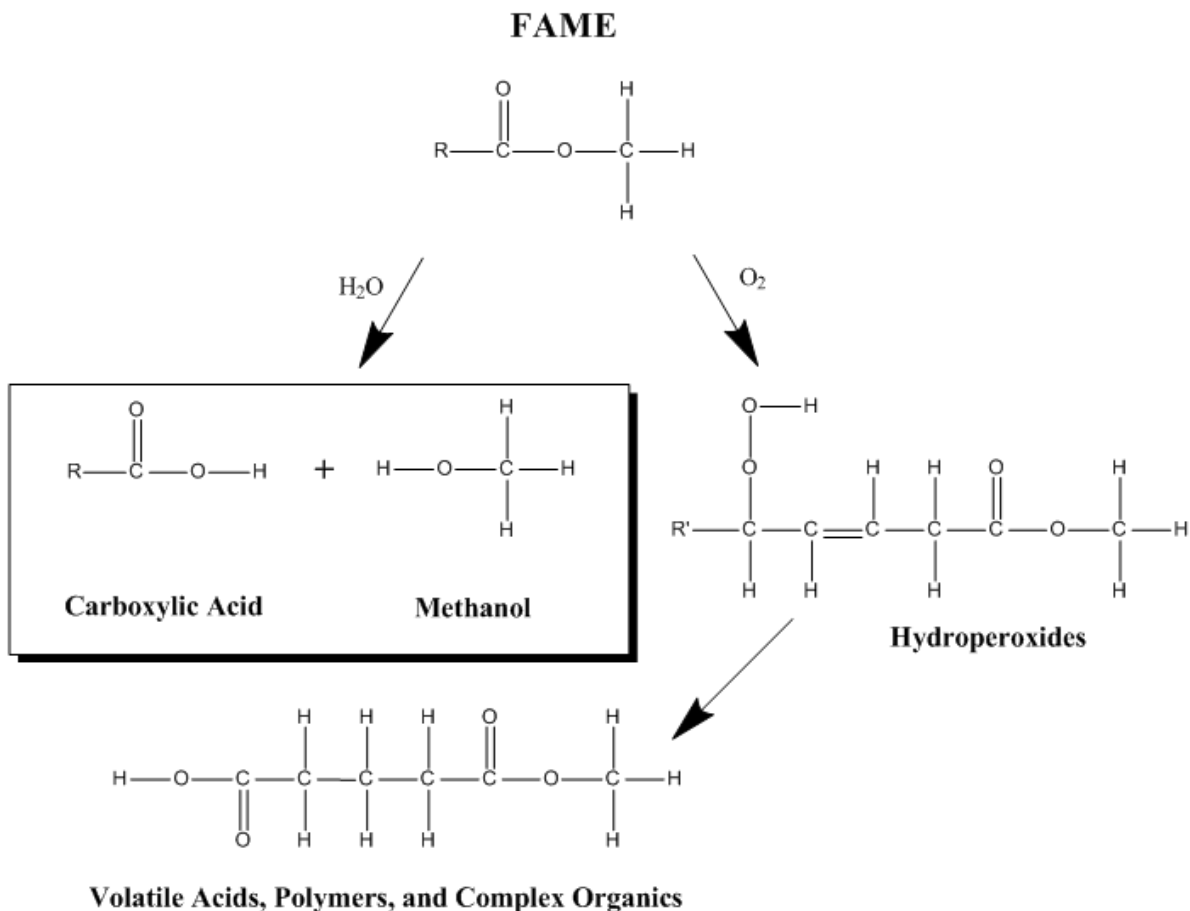


Figure 2-1: Common reaction pathways for fatty acid methyl esters (FAME) [32, 33]

Previous research has shown that the two largest factors influencing the rate of biodiesel oxidation are the temperature and surface area of the fuel exposed to air [22, 34, 35]. These studies have also indicated possible ways of measuring the extent of oxidation. The easiest technique listed was a simple kinematic viscosity test, with viscosity trending upward as fuel oxidizes. Some research suggests a large jump in viscosity when biodiesel is oxidized while others indicate a minimal change. Likely causes for viscosity changes are the formation of polymers at high temperatures, as all of the

research that has shown an increase in viscosity was performed at temperatures exceeding the flashpoint of standard petroleum diesel fuel. Since both acids and peroxides are products of the reaction, acid value (AV) and peroxide value (PV) are the other ways of judging the extent of oxidation. However, since peroxides are an intermediate compound, quickly reacting to form volatile acids, polymers and complex organics the peroxide value is not constant. Therefore the acid value was determined to be the most reliable way to judge the oxidative state of the biodiesel in this research.

2.3.2 Combustion Characteristics of Partially Oxidized Biodiesel

Monyem and Van Gerpen have performed the only documented research on the combustion characteristics of partially oxidized biodiesel [36]. Theory behind the research was that transformation from the original methyl esters to carboxylic acid, peroxides and other oxygen containing compounds carry greater amounts of oxygen into the cylinder in the fuel stream. Results showed that oxidation of biodiesel, both neat and blended, enhanced its ability to act as an oxygenate, reducing CO, THC and PM emissions with no effect on NO_x emissions compared to unoxidized biodiesel and its blends [36].

2.4 Hypothesis and Objectives

Based on the previous research discussed above, additional research is needed to get a more in-depth understanding of fuel property and fuel chemistry changes due to partially oxidized biodiesel. This process would require more detailed analysis of the biodiesel before and after oxidation including kinematic viscosity, flashpoint, the acid value and cetane number and gas chromatography mass spectroscopy analysis. To explore combustion effects of partially oxidized biodiesel both fresh and partially oxidized biodiesel based B20 fuels will be run in a research engine and compared to a baseline neat petroleum diesel fuel. Due to extensive use of EGR in current production diesel engines, the expansion of research over that performed by Monyem and Van Gerpen to include EGR is necessary to

get a real-world picture of the effects of running biodiesel fuel blends containing partially oxidized biodiesel in on-road diesel engines.

Results from these trials will likely yield results that are consistent with previous research, showing decreased products of partial oxidation (THC, CO and PM) with the use of biodiesel blends. Products of partial oxidation will be further decreased by the increased oxygen content in the fuel by blending partially oxidized biodiesel into fuel blends in the place of fresh biodiesel. When EGR is used, similar trends to trials without EGR should be seen only with suppressed NO_x and elevated products of partial combustion compared to trials with the same fuel without EGR.

Chapter 3

EXPERIMENTAL SETUP

3.1 Fuel Preparation and Characterization

3.1.1 Test Fuels

Three different types of fuels were purchased for this research: PC-10 ultra-low sulfur diesel (ULSD), neat soy methyl ester without an additive package (SME) and neat canola methyl ester without an additive package (CME). These three fuels were processed and characterized according to procedures outlined below. After being processed and characterized the fuels were blended into a total of five different fuels to be used in the combustion studies: baseline PC-10 ULSD, fresh SME and CME based B20 fuel blends and partially oxidized SME and CME based B20 fuel blends.

3.1.2 Biodiesel Oxidation Reactor

Biodiesel oxidizes over the course of weeks to months depending on the oxidative stability inherent from the parent oil, processing or additive package associated with the fuel. For fuel testing purposes the biodiesel must be able to be prepared on demand in a timely manner to be utilized before measured fuel properties change. Previous research has shown that the two largest factors influencing biodiesel oxidation are temperature and surface area exposed to air or oxygen. To expedite the process of biodiesel oxidation as much as possible a reactor was constructed to simultaneously heat the fuel to 60°C and bubble pure oxygen through it under 7 kPa gauge pressure. The oxidation reactor shown in figures 3-1 and 3-2 can process 15 liters of fuel per batch in a way that can be considered a well-stirred reactor, providing a high degree of mixedness.

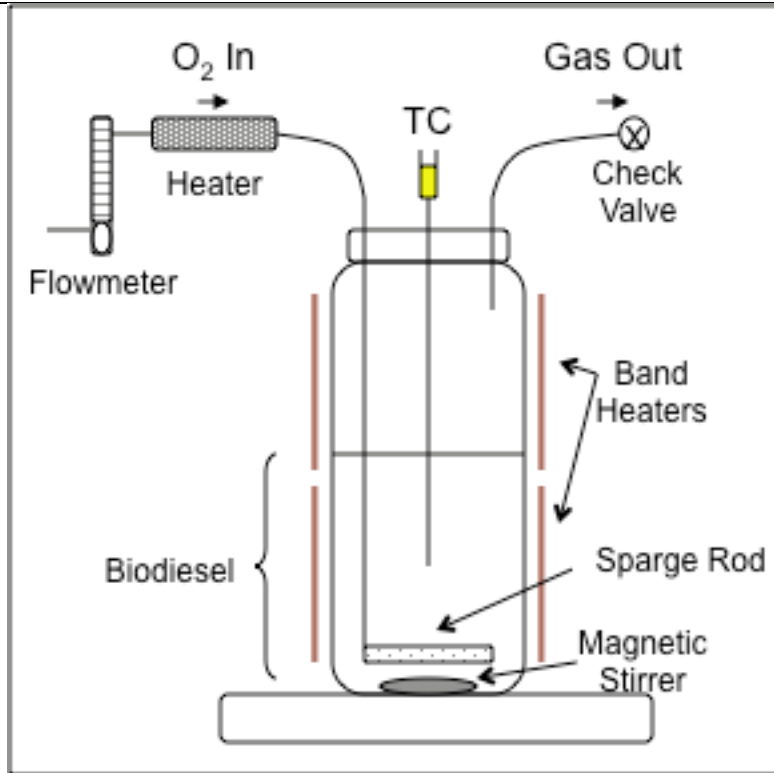


Figure 3-1: Biodiesel Oxidation Reactor Schematic

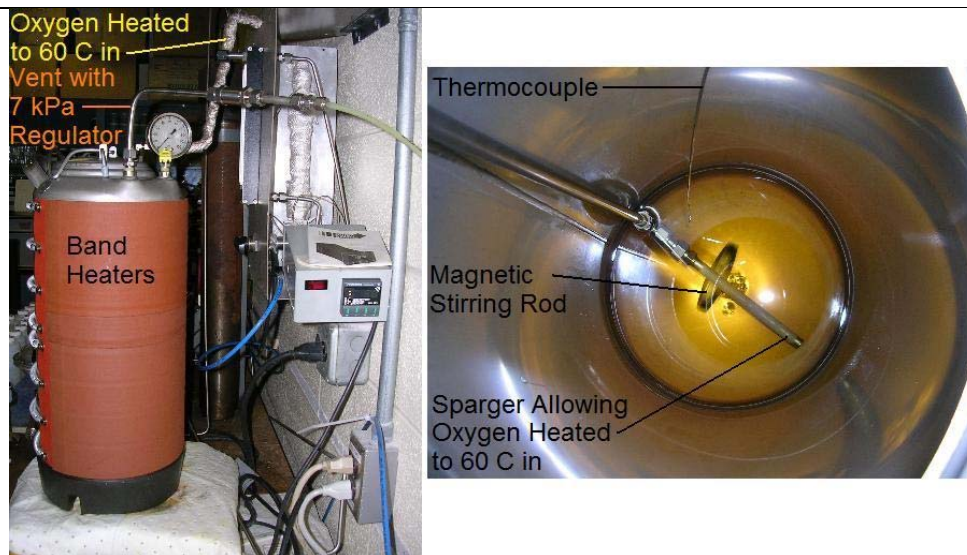


Figure 3-2: Biodiesel Oxidation Reactor

Figure 3-3 clearly shows a high degree of mixing from the magnetic stirring rod further enhanced by the addition of 1 standard liter per minute (slpm) of pure oxygen.



Figure 3-3: High degree of mixing in the oxidation reactor

The procedure to oxidize the fuel was first to allow the fuel to come up to temperature and then oxidize for 6 hours with 1 slpm of heated oxygen bubbling through it. After 6 hours at 60°C the reactor and oxygen flow were turned off and the fuel and reactor were allowed to cool overnight. The following day the stirring rod was turned on for 15 minutes to homogenize the mixture before a sample of the fuel was taken. This was repeated for both canola methyl ester (CME) and soy methyl ester (SME) until each fuel was oxidized at 60°C for 24 hours, resulting in 5 total samples of each fuel.

3.1.3 Fuel Characterization

A total of five tests were performed to both judge the extent of biodiesel oxidation as well as to measure fuel characteristics important to combustion performance. The simplest property change to measure is the kinematic viscosity. A well-stirred 20 liter glass tank with a mixture of 50% water and 50% ethylene glycol is heated to 40°C. Then a glass capillary viscometer is suspended with 10ml of fuel contained in it and allowed to come to temperature over the course of twenty minutes. Finally, fuel is drawn up through the capillary and the time is measured that it takes for the gravity to pull the surface of the fuel between two lines on the capillary. The resulting gravity driven laminar velocity of the fluid gives an extremely accurate value for the kinematic viscosity of the fuel.

Previous observations have shown that as biodiesel oxidizes the peroxides and other volatile compounds that are formed cause the CN to increase. To measure the cetane number of the original and oxidized fuel, an ignition quality test (IQT) is used according to ASTM D 6890 to obtain the derived cetane number. The IQT heats a volume of high pressure standard air to a set temperature, calibrated daily to coincide with standards, and injects a sample of the fuel into the heated chamber. Ignition delay of the fuel is measured based on the pressure rise of the air volume. After being compared to hexadecane (cetane number of 100) and alpha methyl naphthalene (cetane number of 0), the derived cetane number of the fuel can be reported.

The flashpoint is defined as the temperature at which the vapor pressure of the fuel is adequate that it will ignite when an ignition source is introduced. To test the flashpoint, one milliliter of the sample is placed in a metal cup and placed in a closed cup flashpoint testing apparatus. The temperature of the fuel slowly increases and at preset intervals a spark occurs just above the surface of the liquid fuel. When a pressure rise occurs within the cup indicating ignition of the fuel vapors the

temperature is recorded as the flashpoint. Biodiesel's flashpoint, much like its cloud point, has been seen to be much higher than petroleum diesel.

Acid value (AV) is the most complex test that has shown promise to judge the extent of biodiesel oxidation. It involves wet chemistry techniques to measure the mass of potassium hydroxide required to neutralize the acids contained in one gram of fuel. Acid value is measured by first dissolving a measured mass of fuel in a titration solution of high purity isopropanol, toluene and small amount of water. Then according to ASTM standard D 974-97 an indicator solution of naphtholbenzien and titration solution is added followed by a titration of a solution of isopropanol and potassium hydroxide until a neutral solution of fuel and titration solution is indicated. The acid value was reported in units of milligrams of potassium hydroxide per gram of fuel.

Finally, gas chromatography mass spectroscopy (GCMS) testing will be performed on the fuel to detect any changes in composition. GCMS identifies chemical compounds through a combination of boiling point, polarity and molecular structure. By comparing GCMS results from neat fresh SME and CME with neat partially oxidized SME and CME it is hoped that trace chemicals that evolve in the oxidation process will be seen. The most probable change that will be seen is small peaks that appear to each side of the main peaks of the fresh fuel. These would represent slightly heavier peroxides forming as an intermediate species and final species that include heavier organic polymers and lighter volatile species. Using the mass spectroscopy library the computer connected to the GCMS should be able to identify any extra compounds that appear during oxidation.

3.2 Engine Testing

3.2.1 Research Engine

Engine testing was carried out using a single cylinder air cooled naturally aspirated Yanmar model L70EE direct injection diesel engine. This small displacement engine was chosen due to its low fuel consumption, simplicity and high brake-specific emissions. Low fuel consumption allows for many different running conditions to be explored while using the exact same batch of oxidized fuels, minimizing variables if any trends are observed to change using the same fuel. Simplicity and high brake-specific emissions act to also minimize the variables that can enter into the study and to also make small variations such as intake air temperature or humidity insignificant in the overall brake-specific emissions. The engine, shown in figure 3-3, was connected to a computer controller run through LabVIEW and an eddy current dynamometer. Simultaneous measurement of the engine torque and speed entered into a negative feedback control loop allow for accurate engine control and brake-specific emissions measurement.

A custom liquid cooled exhaust gas recirculation loop was installed on the engine that allows for up to 17% EGR use in the engine. Pictured in figure 3-4, it has temperature controlled automotive coolant circulating through the heat exchanger that is located directly after the valve that controls the amount of exhaust that is allowed back in the intake of the engine. By cooling the exhaust before sending it back in the intake, it helps to decrease the volume flow rate of exhaust allowing for higher power outputs with the same EGR levels.

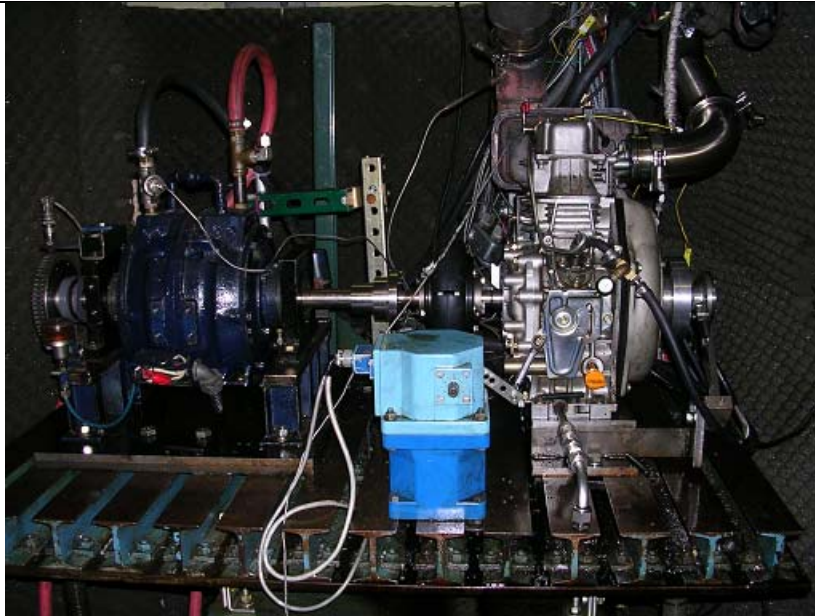


Figure 3-4: Yanmar L70EE diesel engine (right) connected to the eddy current dynamometer (left)

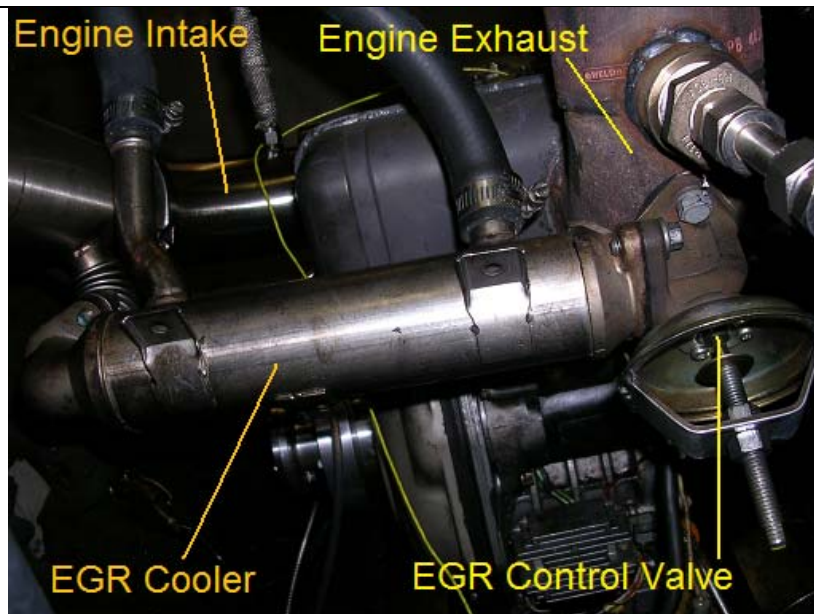


Figure 3-5: Custom EGR loop installed on Yanmar research engine

3.2.2 Emissions Equipment

An AVL emissions bench was utilized to monitor THC, CO, NO_x, nitric oxide (NO) and carbon dioxide emissions. The bench was first calibrated by circulating zero gasses followed by span gasses with higher concentrations of pollutants than would be exhausted from the engine to give a linear calibration of the sensors within the range of engine operations. The AVL bench was connected to the intake and exhaust of the Yanmar diesel engine by heated emissions sample lines to avoid condensation of water and gaseous hydrocarbon emissions. Headline filters were also installed at the connection points on the intake and exhaust of the engine in order to filter any PM out of the sample being collected. Once CO, NO_x, NO, THC and carbon dioxide emissions are collected for each trial, the PM emissions data must be collected and analyzed.

A Sierra Instruments model BG-3 particulate partial flow sampling system was utilized to collect samples of the particulate being emitted from the engine. The fiberglass based filters were first allowed to come to steady-state humidity over the course of 48 hours in a fixed 45% relative humidity chamber and weighed to the nearest microgram. Sampling was performed for five minutes with an exhaust flow of 7.5 slpm diluted with 67.5 slpm of temperature controlled air through the BG-3, resulting in a 10:1 dilution ratio. Filters were again allowed to come to steady-state at 45% relative humidity before being weighed again. From the samples the brake-specific total PM emissions can be calculated. Particulate matter samples collected by the BG-3 can then also go on to be solvent extracted overnight with dichloromethane to derive the brake-specific soluble and insoluble PM that makes up the total PM. Knowledge of the proportions of soluble and insoluble PM in the sample can help provide insight into the mechanisms that cause any trends seen with the PM.

3.3 Statistical Analysis

Error was calculated for all data assuming a 95% confidence interval and that all error was random and independent. According to techniques outlined by Moffat the error to each side of the average was calculated as one standard deviation of the data multiplied by the corresponding T-distribution value and then divided by the square root of the number of samples [37].

Chapter 4

FUEL CHARACTERIZATION

4.1 Fuel Preparation for Engine Testing

The baseline ultra-low sulfur petroleum diesel (ULSD) fuel was represented by PC-10 fuel developed and specified for lubricant certification testing. Both SME and CME were blended in at B20 ratios with PC-10 for iteration and confirmation of any results. No larger ratios were used because of biodiesel fuel blend specifications set forth by the Energy Policy Act (EPAAct) of 2005.

Neat soy and canola biodiesel were oxidized for a total of twenty four hours at 60°C at 7 kPa gauge pressure under a pure oxygen atmosphere. Samples were drawn every six hours to detect trends as the oxidation of the biodiesel progressed. These partially oxidized versions of SME and CME were also blended with PC-10 at B20 ratios, creating a total of five different fuels to be run in the engine: PC-10 petroleum diesel, B20 made from new soy biodiesel, B20 made from partially oxidized soy biodiesel, and both new and partially oxidized canola based B20.

4.2 Observations

Immediate observations yielded a definite color change comparing virgin fuel with fuel that has been oxidized for 24 hours. Oxidation of soy methyl ester caused the fuel that started out clear to turn a very light brown. The SME was purified using a distillation technique therefore it can be concluded that reactions involving trace impurities left over after fuel purification is not to blame for the color change. However trace compounds produced during the partial oxidation of the fuel could have caused the

observed color change. CME experienced a similar slight color change from an orange color to a yellow color when comparing the as received fuel will fuel after being oxidized for 24 hour. A more in-depth analysis of each fuel must be performed through kinematic viscosity (ν), derived cetane number (CN), acid value (AV), and gas chromatography mass spectroscopy (GCMS) testing to determine the exact cause for the change.

4.3 Kinematic Viscosity

There were no large changes in viscosity of either biodiesel fuel to report. Pure soy methyl ester (SME) showed no statistically significant viscosity change over the course of the 24 hour total oxidation time, as shown in figure 4-1. Meanwhile the pure canola methyl ester (CME) showed a statistically significant 2% increase in viscosity, shown in figure 4-2, after being oxidized for 24 hours.

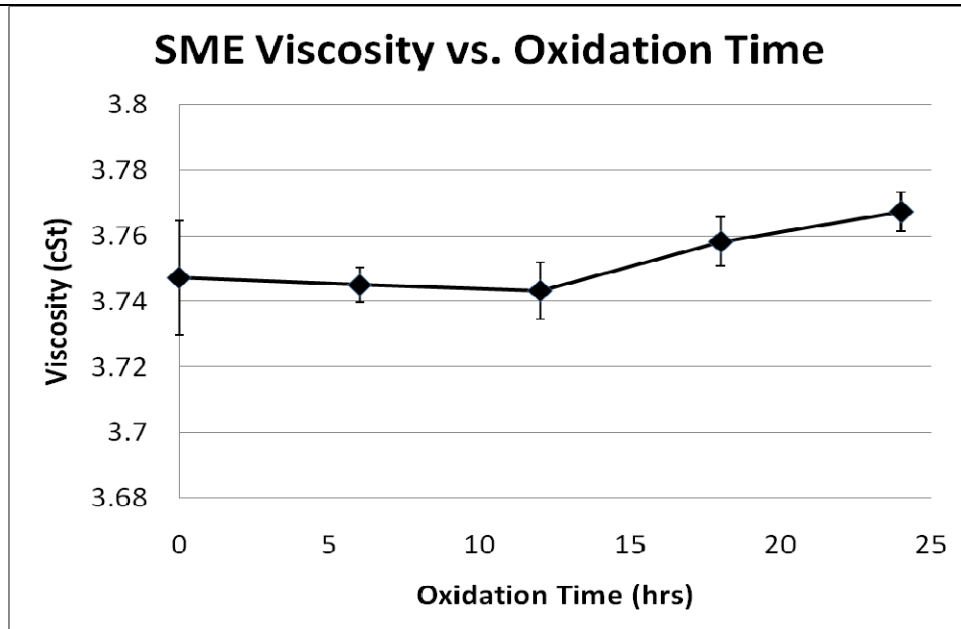


Figure 4-1: Soy methyl ester viscosity change with respect to oxidation time.

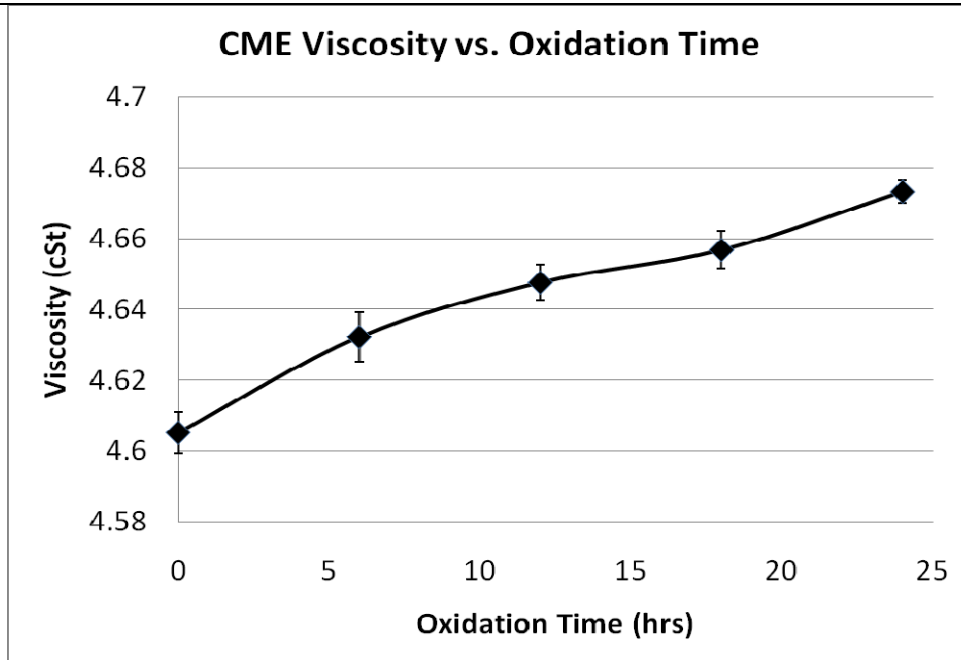


Figure 4-2: Canola methyl ester viscosity change with respect to oxidation time.

Results from the viscosity measurement of the fuels show that compared to the PC-10 petroleum diesel with a viscosity of 2.41 cSt, the un-oxidized SME and CME are 56% and 91% more viscous in neat form respectively. When blended with PC-10 at levels of 20% biodiesel and 80% petroleum diesel (B20), the higher viscosity of biodiesel increased the viscosity of the fuel by 0.20 cSt for SME based B20 and 0.32 cSt for CME based B20. This means that the maximum increase of 0.08 cSt for neat (100%) biodiesel after oxidation was insignificant compared to the change of viscosity from blending any type of biodiesel with the petroleum diesel. Error in measurements during these trials was maintained well below 1% of the values measured. A reason why the viscosity change was not observed to be as significant as other research was because of the closed oxidation reactor barring any volatile compounds from escaping. All previous research that indicated a significant viscosity increase used an

open-air reactor allowing volatile compounds formed during partial oxidation to evaporate, leaving more viscous heavy ends in the liquid fuel sample [22, 35].

4.4 Flashpoint

Flashpoints of fuel can help to provide insight into data trends that emerge from compression ignition (CI) engine testing. A change in the flashpoint of a fuel can indicate that the fuels volatility has changed. Higher volatility leads to more fuel components becoming vaporized at a given temperature leading to a shorter physical ignition delay as well as a smaller liftoff length from the fuel injector.

Figure 4-3 shows that there were no statistically significant changes other than a 1.5% decrease of the flashpoint for SME after 24 hours of oxidation compared to completely un-oxidized SME.

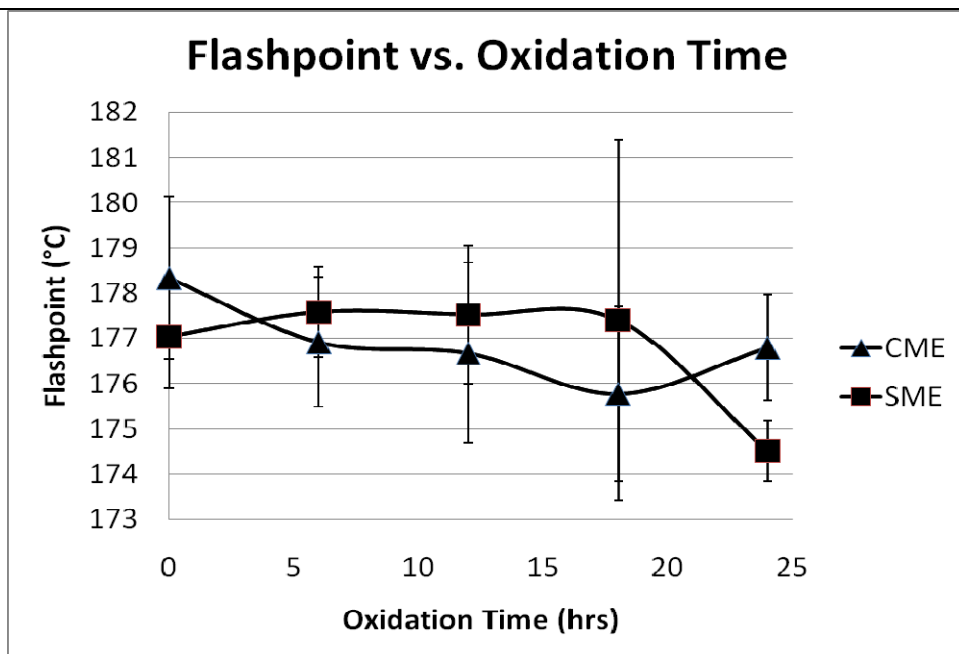


Figure 4-3: Flashpoint of SME and CME with respect to oxidation time

Due to the extreme reactivity of peroxides formed in biodiesel, the decreased flashpoint of SME at 24 hours of oxidation could point to a high rate of oxidation after an initiation period without significant oxidation having taken place. CME on the other hand may have already passed this initiation period because of its greater age when being put into the oxidation reactor at zero hours of oxidation. Constant, slow reaction throughout the oxidation time drove the CME to higher viscosity without a high peroxide value at any time, leading to a more consistent flashpoint. One key piece of data to keep in mind is that the flashpoint of both SME and CME are statistically the same until 24 hours of oxidation. Therefore if similar trends were seen with the non-oxidized fuels but different trends were seen with oxidized fuels, mechanisms involved with the flashpoint could be involved with those changes of emissions.

4.5 Acid Value

Final products of biodiesel degradation commonly include volatile acids. The acid value of a fuel measures the amount of acids by finding the mass of potassium hydroxide (KOH) required for neutralizing one gram of fuel. Results of the acid value testing showed that both the SME and CME had statistically significant increases in acid number over the course of 24 hours of oxidation in the biodiesel reactor. Figure 4-4 clearly shows that the SME used in the oxidation trials did not oxidize as quickly as the CME with only an 8% increase in acid number compared to the 44% increase shown for the CME.

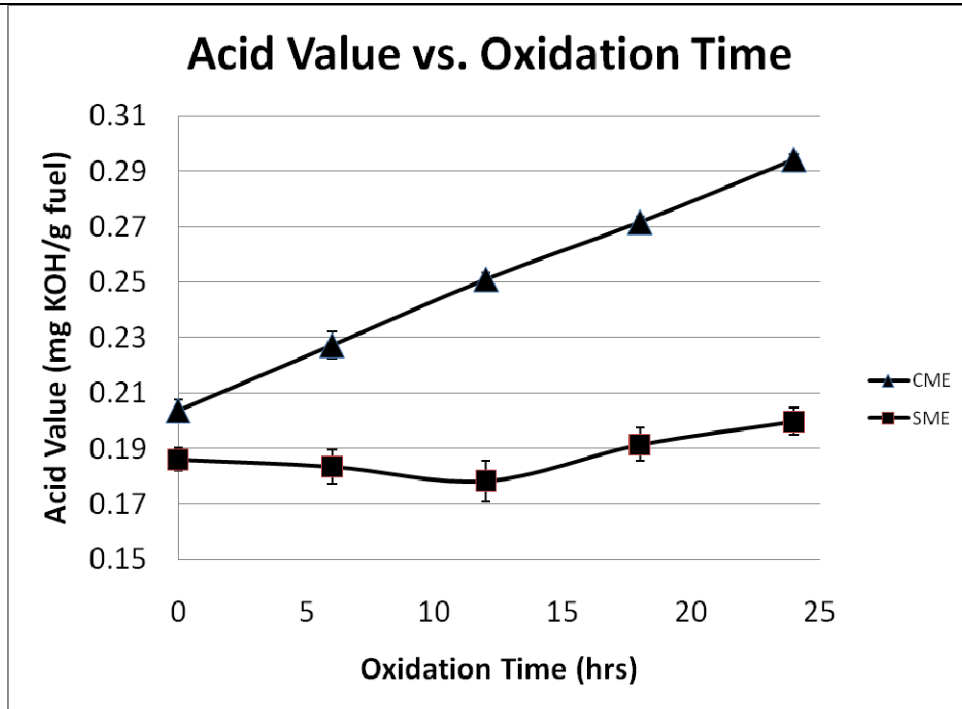


Figure 4-4: Acid value change with respect to oxidation time

Consistency can be seen between the acid value and viscosity data. The kinematic viscosity and acid value of the SME can be seen to drop until 18 hours of oxidation, after which it began to increase. Acid value and viscosity of the CME can also be seen to match, nearly linearly ramping upward in both cases. The peculiar trend seen with the SME was not statistically significant but since it occurred with both properties, it gives merit to linking the two properties as both indicating similar reactions in the fuel. Acid value is preferred over kinematic viscosity however because the same change in the fuel causes a 44% change in acid value compared to a 7% change in viscosity as seen with the CME, so it is much more sensitive.

4.6 Cetane Number (CN)

Measuring the ignition delay of a fuel under controlled conditions can yield valuable insight into fuel chemistry in a CI engine, commonly quantified by the cetane number of a fuel. Small changes in the fuel composition can cause large changes in the type and rate of radical formation that is key to the ignition and combustion of fuels. Biodiesels are well known to have elevated CNs compared to most petroleum diesel fuels. Partially oxidized or aged biodiesels are much less studied leading to the need for data showing how the CN of biodiesel changes with respect to oxidation time. Results showing the CN change with respect to the oxidation time of SME and CME are shown in table 4-1.

Table 4-1: Cetane number of PC-10 Ultra-low Sulfur Diesel, SME and CME with respect to oxidation time

	0 Hours	24 Hours
PC-10 ULSD	40.3	-
Soy Methyl Ester	49.8	57.9
Canola Methyl Ester	65.7	72.1

4.7 Gas Chromatography Mass Spectrometry (GCMS)

Due to the change in acid number and cetane number of both the soy and canola methyl ester fuels it is evident that a chemical reaction has progressed and formed new compounds. By using the GCMS it was hoped that new chemical “peaks” would be seen suggesting that a significant chemical composition change occurred. Baseline curves showing the composition of both SME and CME can be seen in figure 4-5 and 4-6. Relative concentrations of different fatty acid methyl esters in our fresh SME and CME closely mimic the relative composition of different fatty acid methyl esters listed for soy and rape, which is the same as canola, methyl ester listed in table 4-2.

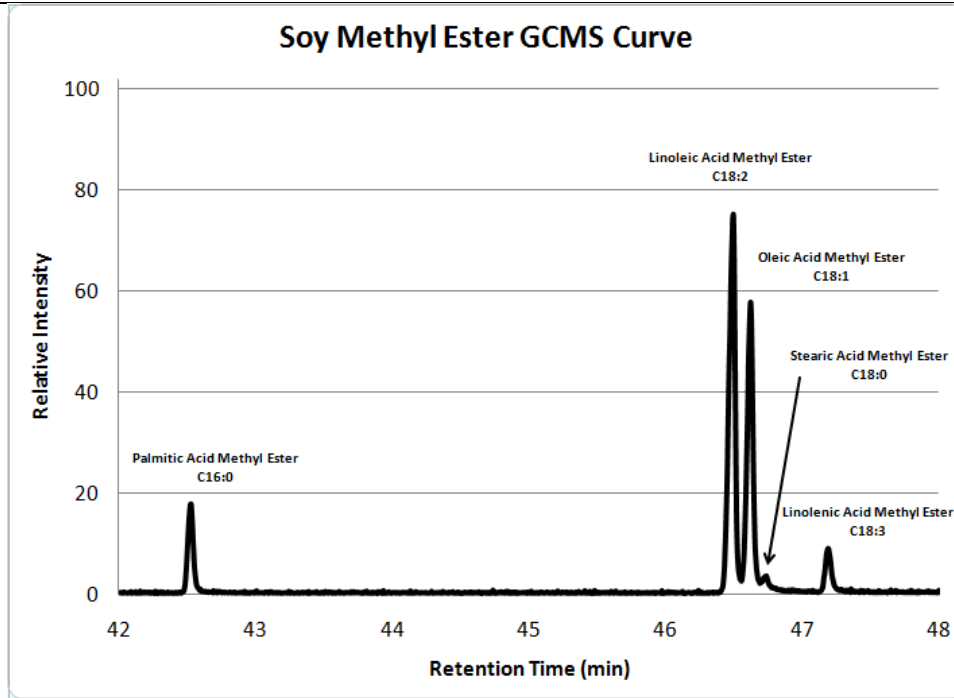


Figure 4-5: GCMS curve for new soy methyl ester

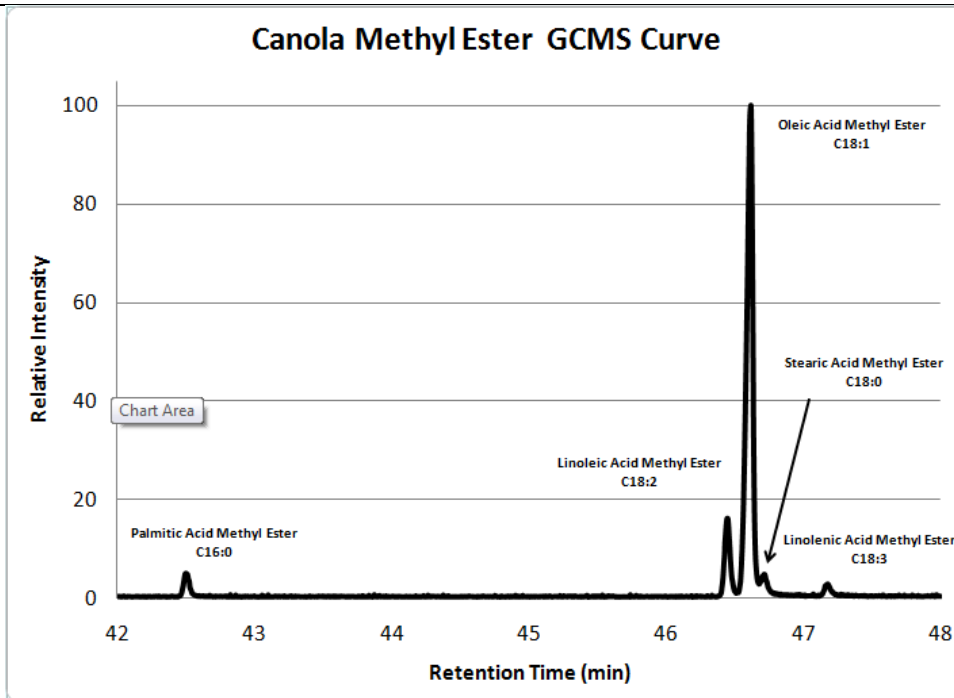


Figure 4-6: GCMS curve for new canola methyl ester

Table 4-2: Composition of Various Biodiesels [19]

Fatty acid		Palm	Olive	Peanut	Rape	Soybean	Sunflower	Grape	H.O. Sunflower	Almond	Corn
Lauric	C12:0	0.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Myristic	C14:0	0.7	0.0	0.1	0.0	0.0	0.0	0.1	0.0	0.0	0.0
Palmitic	C16:0	36.7	11.6	8.0	4.9	11.3	6.2	6.9	4.6	10.4	6.5
Palmitoleic	C16:1	0.1	1.0	0.0	0.0	0.1	0.1	0.1	0.1	0.5	0.6
Stearic	C18:0	6.6	3.1	1.8	1.6	3.6	3.7	4.0	3.4	2.9	1.4
Oleic	C18:1	46.1	75.0	53.3	33.0	24.9	25.2	19.0	62.8	77.1	65.6
Linoleic	C18:2	8.6	7.8	28.4	20.4	53.0	63.1	69.1	27.5	7.6	25.2
Linolenic	C18:3	0.3	0.6	0.3	7.9	6.1	0.2	0.3	0.1	0.8	0.1
Arachidic	C20:0	0.4	0.3	0.9	0.0	0.3	0.3	0.3	0.3	0.3	0.1
Gadoleic	C20:1	0.2	0.0	2.4	9.3	0.3	0.2	0.0	0.0	0.0	0.1
Behenic	C22:0	0.1	0.1	3.0	0.0	0.0	0.7	0.0	0.7	0.1	0.0
Erucic	C22:1	0.0	0.0	0.0	23.0	0.3	0.1	0.0	0.0	0.0	0.1
Lignoceric	C24:0	0.1	0.5	1.8	0.0	0.1	0.2	0.0	0.3	0.2	0.1
Nervonic	C24:1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.4	0.0

The only outlier from the expected trend in the retention time was the linolenic acid methyl ester (C18:3) which would be expected to have a shorter retention time than linoleic acid methyl ester (C18:2) due to its lighter molecular weight. However, linolenic acid methyl ester is extremely reactive with oxygen, so it can be expected that any linolenic acid methyl ester contained in the fuel would react within a matter of hours to days: forming other more stable compounds. In the case of fatty acid methyl esters (FAMES) these more stable compounds can include peroxides, volatile acids, polymers or other complex organic molecules.

Pictured below in figures 4-7 and 4-8 are the gas chromatography mass spectrometry curves for partially oxidized biodiesel—showing no additional peaks. However, due to the close molecular weight and structure of the products of partial oxidation, the emerging peaks could be obscured by existing peaks of the original FAMES. Without certain identification of new compounds from partial oxidation, one certain trend with partially oxidized fuels was increased oxygen content that routinely result in lower emissions of incomplete combustion and diesel particulate matter. This hypothesis was tested

next with research engine testing of soy and canola biodiesel blended into PC-10 ULSD fuel at levels of twenty percent by volume (B20) and compared to partially oxidized biodiesel in B20 blends.

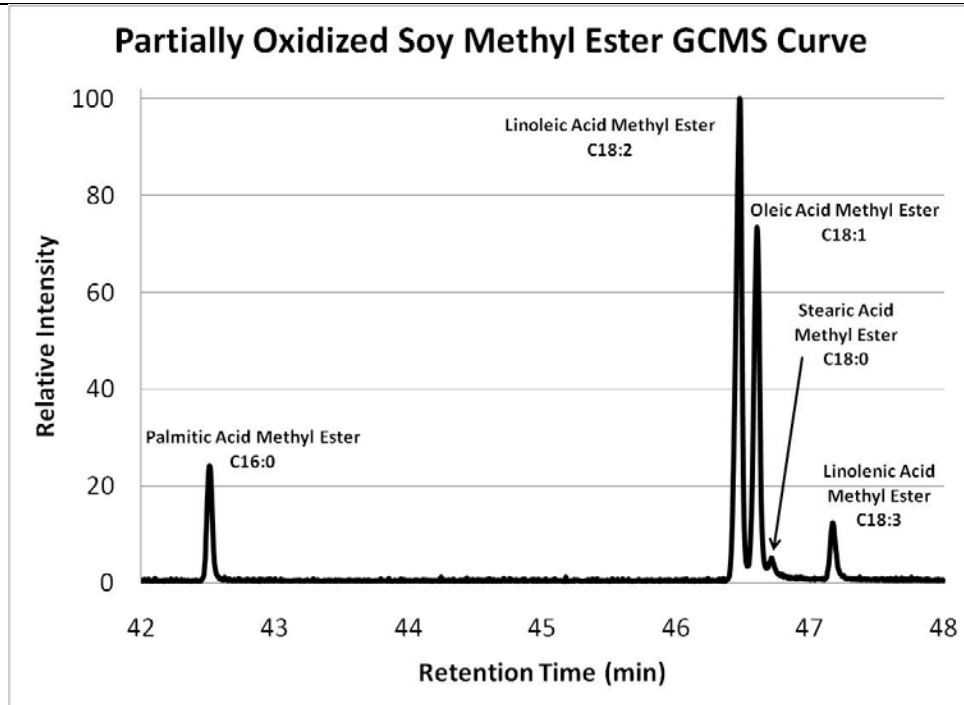


Figure 4-7: GCMS curve for soy methyl ester after 24 hours of oxidation

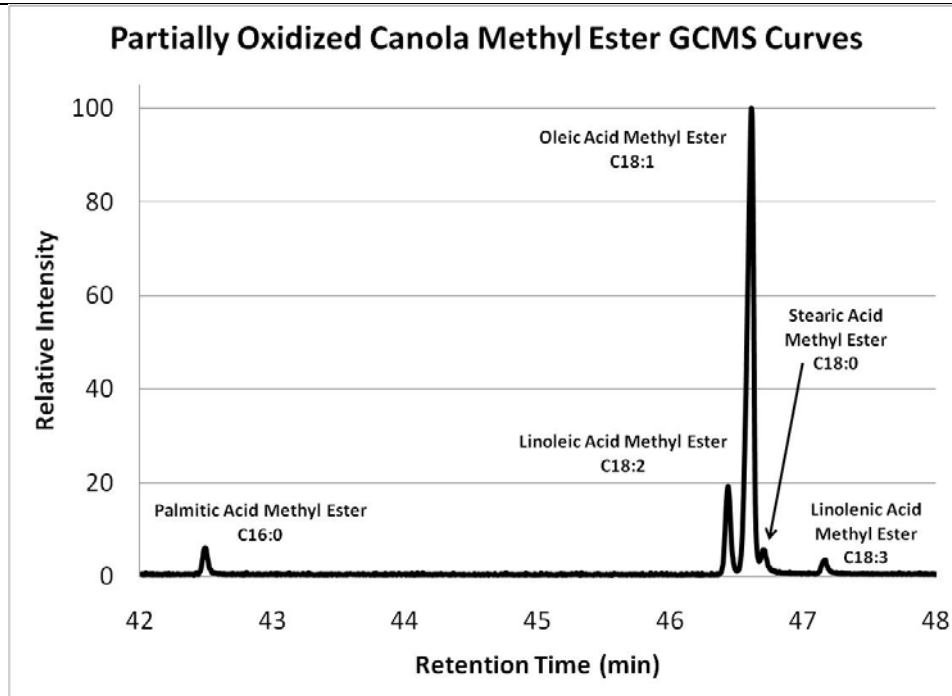


Figure 4-8: GCMS curve for soy methyl ester after 24 hours of oxidation

Chapter 5

ENGINE TESTING RESULTS

5.1 Total Hydrocarbon (THC) Emissions

Hydrocarbon emissions from internal combustion engines are mitigated by catalysts in the exhaust system. Any unburned hydrocarbons being emitted by an engine however do result in a loss of efficiency by not liberating all the chemical potential energy introduced into the engine in the form of fuel. The use of EGR in compression ignition engines running standard fuel is commonly seen to increase many incomplete combustion products of unburned hydrocarbons and carbon monoxide by decreasing peak combustion temperatures. Previous research has also shown that biodiesel blending with petroleum diesel results in a reduction of THC emissions [21].

In the Yanmar test engine, hydrocarbon emissions increased with the use of petroleum diesel and EGR and decreased with the use of a biodiesel blend was observed. Combined use of a biodiesel fuel blend and EGR further decreased the THC emissions beyond that observed with just the addition of biodiesel in some cases. Figure 5-1 shows that partially oxidized biodiesel showed the same trend in total hydrocarbon emissions as regular biodiesel, but with an overall statistically significant decrease. Consistency could be seen between SME and CME based B20 fuels, both new and partially oxidized, with a decrease when running with 10% EGR and an overall decrease when partially oxidized biodiesel is added to the blend.

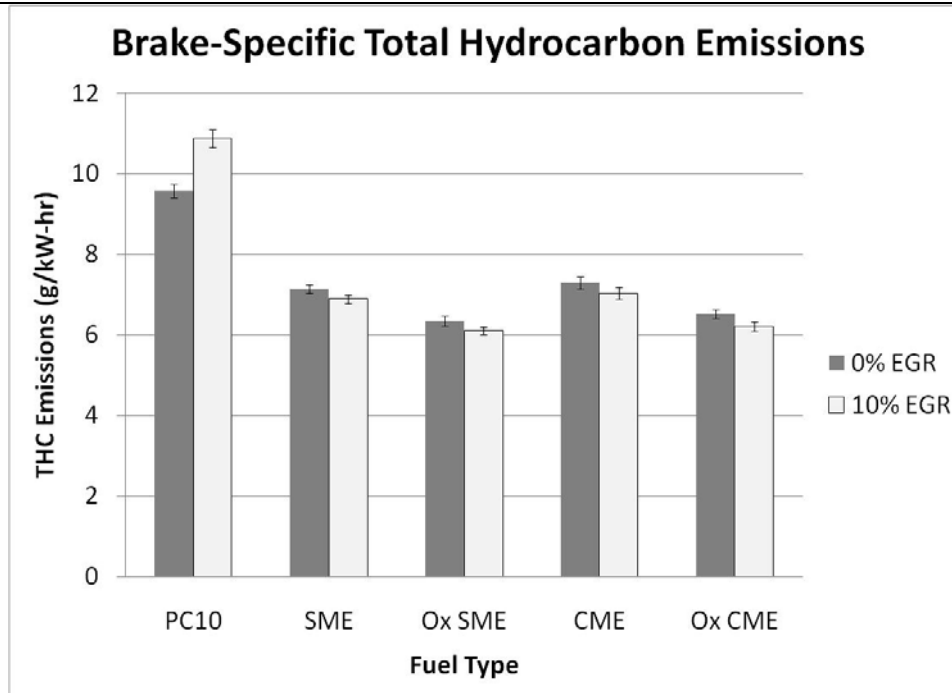


Figure 5-1: Brake-specific total hydrocarbon emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

By adding 10% EGR there is a statistically significant 13.6% increase in THC emissions when running on PC-10 petroleum diesel. Compared to this, while running on all types of B20, there was a drop of between 3 and 5% in THC emissions. The impact of the oxidized biodiesel is very apparent with an overall decrease between 10 and 12% in THC emissions. All figures are statistically significant and indicate a much stronger influence from oxidized biodiesel being added to the engine than 10% EGR.

5.2 Carbon Monoxide (CO) Emissions

Products of incomplete combustion also include carbon monoxide. As was the case with unburned hydrocarbon emissions carbon monoxide emissions are very easily cleaned up from the exhaust of an internal combustion engine through the use of an oxidation catalyst. The main sources of carbon monoxide emissions from internal combustion engines is localized fuel rich conditions in the cylinder and bulk quenching at the end of the combustion process [6]. In direct injection compression ignition engines, localized fuel rich conditions occur in the fuel rich regions within the fuel spray. Oxygen poor surroundings can also cause faster bulk quenching in the cylinder resulting in higher carbon monoxide emissions with the addition of EGR, as seen in figure 5-2.

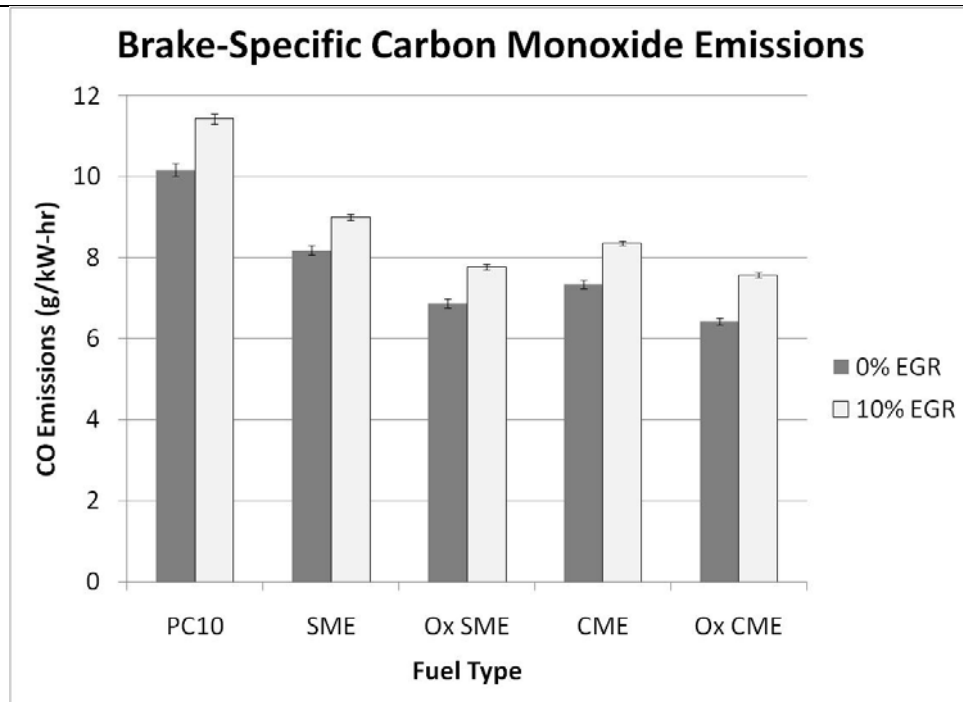


Figure 5-2: Brake-specific carbon monoxide emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Using partially oxidized biodiesel in B20 fuel blends is also shown to significantly reduce CO emissions, even compared to fresh biodiesel. Brake-specific CO emissions rose between 10 and 18% with the use of 10% EGR compared to running the engine without EGR. The addition of partially oxidized biodiesel showed a statistically significant downward trend compared to unoxidized biodiesel. Reductions caused from the use of partially oxidized biodiesel ranged from 10 to 16%. This shows that partially oxidized biodiesel in B20 blends has approximately the same magnitude but opposite effect on CO emissions that 10% EGR does. This means that higher levels of EGR can be used in an engine fueled with partially oxidized biodiesel based B20 to lower NO_x levels without the need for a larger DOC to neutralize elevated CO emissions.

5.3 Brake-Specific Fuel Consumption (BSFC) and Carbon Dioxide Emissions

Two of the main concerns when evaluating modern internal combustion engines are brake-specific fuel consumption and carbon dioxide emissions. Reasons for the concern are due to the rising cost of liquid transportation fuels and mounting concern over global climate change respectively. The two are linked due to the fact that most liquid fuels for compression ignition engines are similar in their elemental composition—leading to a link between the mass of fuel consumed and the mass of carbon dioxide emissions. Changes to fuel consumption and carbon dioxide emissions are also related to the overall efficiency of the engine making injection and ignition timing especially important when considering compression ignition engines. By increasing efficiency, and thereby lowering BSFC and carbon dioxide emissions, the engine's impact on global warming can be lessened when running on petroleum-based fuel.

Trends in figure 5-3 show that SME had slightly higher fuel consumption without EGR due to the lower energy density of biodiesel requiring more fuel to put out the same power. SME with 10% EGR did not show as high of fuel economy penalty as PC-10 with 10% EGR due to the higher oxygen content of the fuel helping to offset the effects of EGR. When running with both fresh and partially oxidized CME based B20 fuels there were the lowest observed fuel efficiency. The dominating reason for the lowest fuel consumption with CME was due to the highest cetane numbers observed of all the fuels tested, advancing the ignition timing the closest to top dead center, causing the thermodynamic cycle of the engine to become the overall most efficient.

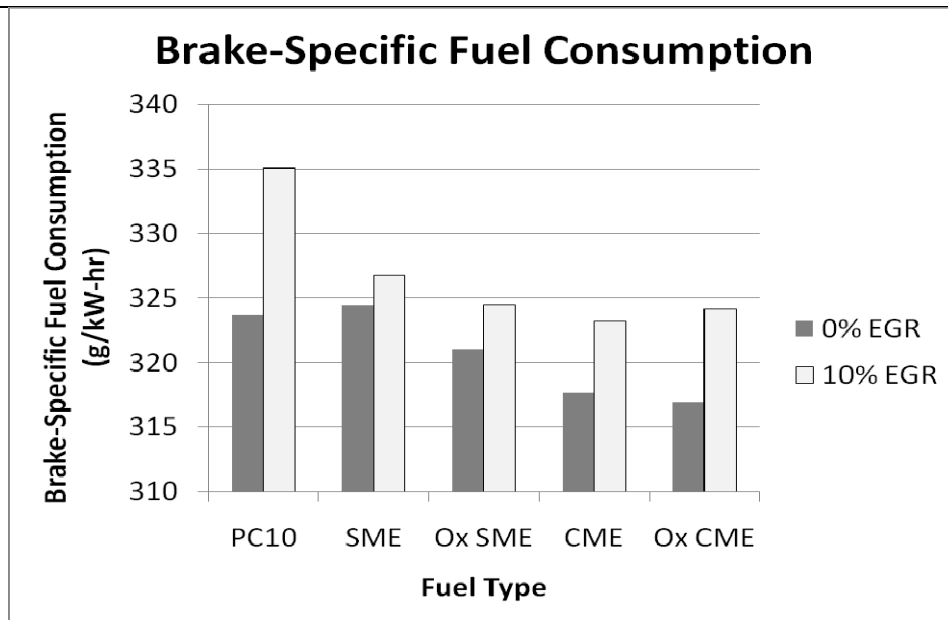


Figure 5-3: Brake-specific fuel consumption when using PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Brake-specific carbon dioxide emissions reflect the exact trends seen with fuel consumption. In all cases the addition of 10% exhaust gas recirculation caused a statistically significant increase in carbon dioxide emissions. As was the case with fuel consumption, by blending biodiesel in at 20% by volume the carbon dioxide increase using 10% EGR was much less than the observed 5.8% penalty with standard ULSD. Increases with all types of B20 fuels were seen in figure 5-4 to remain between 1 and 3%. The only statistically significant change between new and partially oxidized based B20 fuel were the cases without EGR involving SME based fuel. All other B20 fuels showed no statistically significant change with the addition of partially oxidized biodiesel instead of new biodiesel.

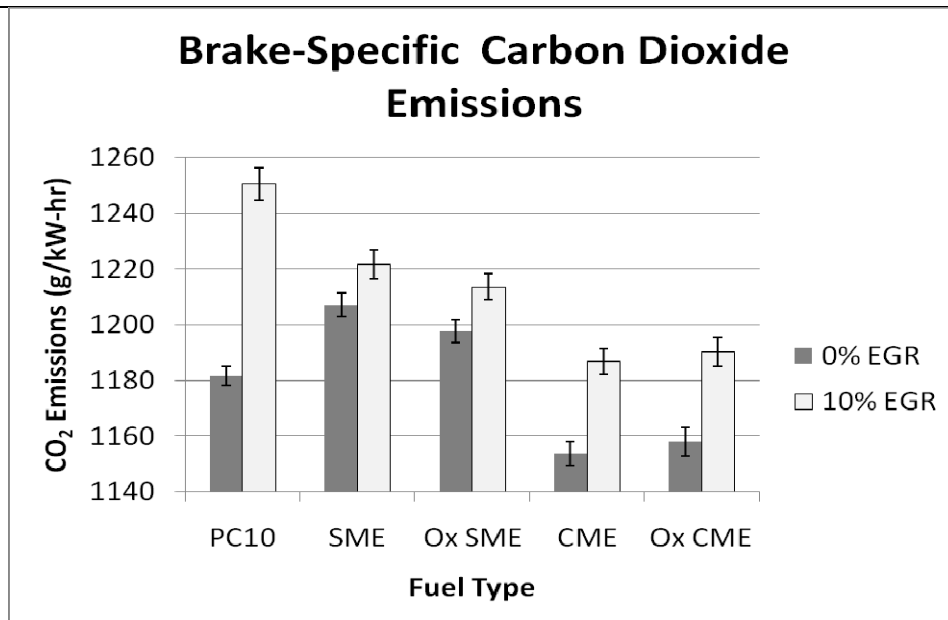


Figure 5-4: Brake-specific carbon dioxide emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

5.4 NOx Emissions

NOx stands for the collective group of oxides of nitrogen, including NO and NO₂. Most NOx is formed through Zeldovich mechanisms, which is why exhaust gas recirculation, creating a higher specific heat and lower concentration of oxygen in the cylinder, is a very common way to control NOx. EGR lowers peak combustion temperatures and the concentration of oxygen decreasing the probability of NOx formation through two ways. Unfortunately through still unclear mechanisms the use of biodiesel in compression ignition engines cause an increase in brake-specific NOx emissions. Figure 5-5 clearly shows the effects of both EGR and biodiesel use in the Yanmar research engine is consistent with research to date, increasing with all types of B20 over the baseline PC-10 fuel and decreasing in all cases with EGR compared to without it [24-26].

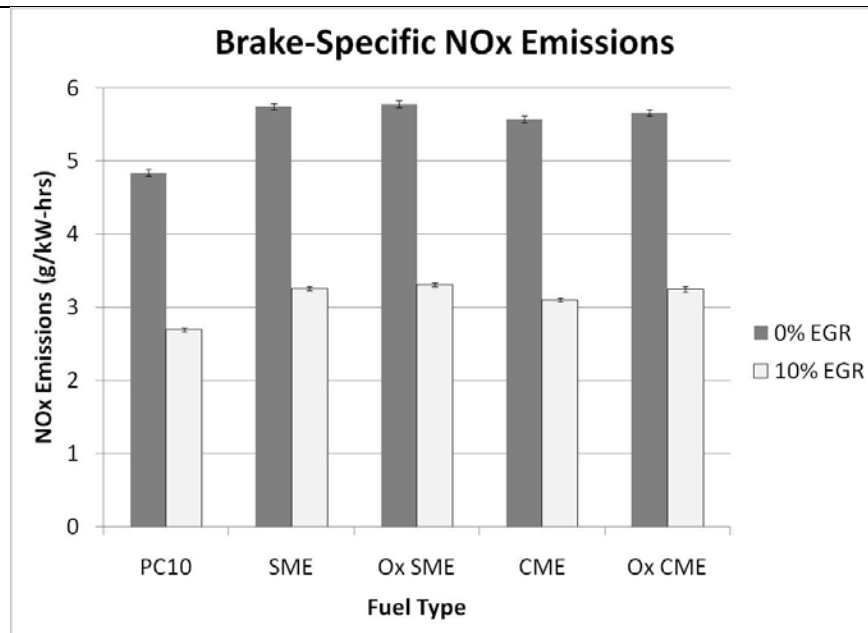


Figure 5-5: Brake-specific NOx emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Figure 5-6 shows that when running without EGR there was a shift in the composition of NOx emissions from over 95% NO when running pure ULSD to between 92 and 93.5% NO when running B20 with the balance being NO₂. With this statistically significant trend it is necessary to examine the composition of NOx emissions when using EGR.

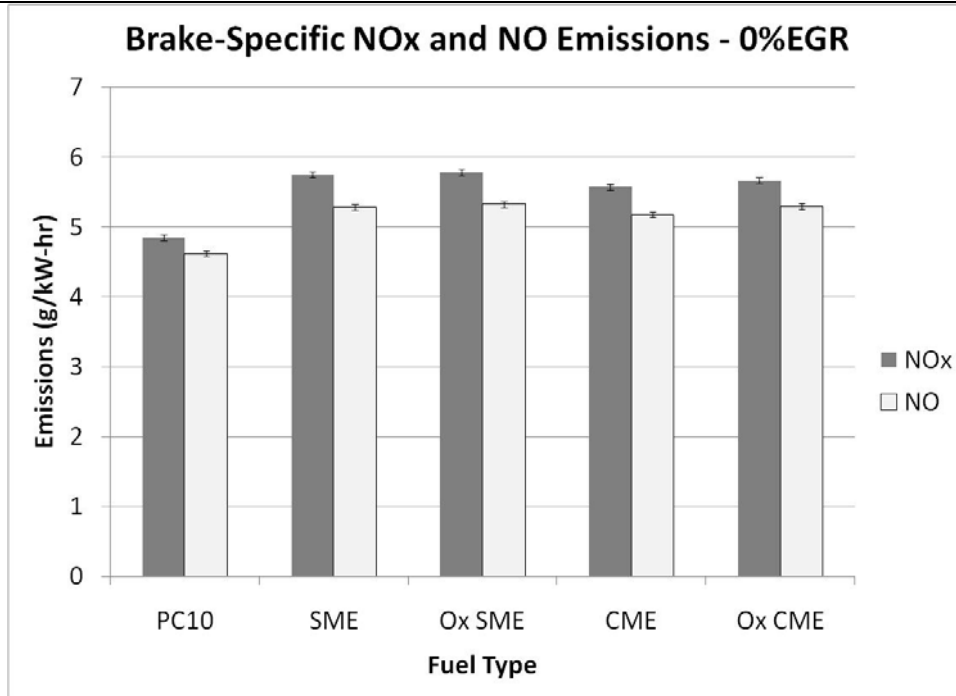


Figure 5-6: Brake-specific NOx and NO emissions without EGR with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Trends observed without EGR remained consistent when 10% EGR was used under the same conditions. NOx emissions for PC-10 were composed of over 95% NO while all B20 blends ranged between 91.7 and 93.7% as displayed in figure 5-7. In the interest of examining the effect of partially

oxidized biodiesel it can also be seen in both figures 5-6 and 5-7 that CME versus partially oxidized CME is the only statistically significant change in NO_x emissions—increasing by 4.7% and 1.6% with and without EGR respectively.

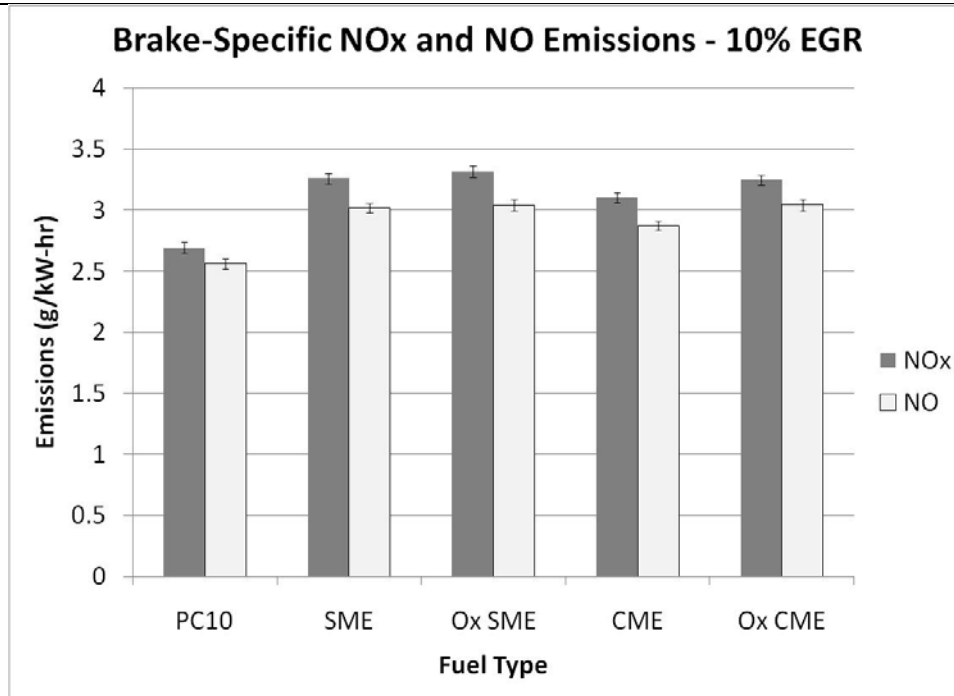


Figure 5-7: Brake-specific NO_x and NO emissions with EGR with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Brake-specific NO₂ emissions were derived from direct measurement of total NO_x and NO emissions and can be seen in figure 5-8. Relatively large error is due to the combination of low concentrations of NO₂ and the addition of error from NO_x and NO measurement to comply with statistically sound techniques of data analysis. No statistically significant trends can be seen with with

NO₂ concerning the use of new versus partially oxidized biodiesel fuel blends. As stated above, there are significantly higher NO₂ emissions with all B20 fuels compared to pure ULSD making PM oxidation more favorable with B20.

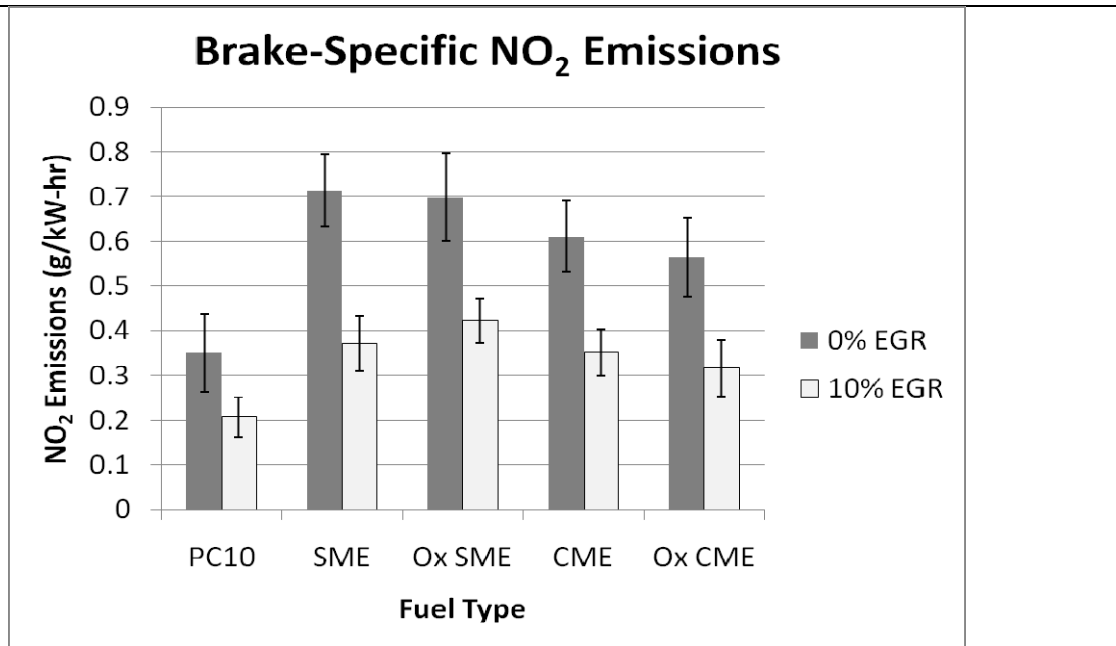


Figure 5-8: Brake-specific NO₂ emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

5.5 Particulate Matter (PM) Emissions

Particulate matter emissions are the other major concern for modern compression ignition engines. Particulate matter emissions are generally composed of two separate states of matter. The most important of these is a solid “insoluble” portion of particulate matter composed mainly of carbon. Exact mechanisms of insoluble particulate matter formation are still unknown but many scientists agree

that the process involves the formation and condensation of polycyclic aromatic hydrocarbons (PAHs) into larger liquid-like precursor particles. Hydrogen abstraction, carbon addition (HACA) is a common way this process is referenced. Individual liquid-like particles then stick together and solidify to form larger aggregate particles composed of many individual solid onion-like layered particles [26, 34].

Total particulate matter measurements were taken using a Sierra Instruments model BG-3 particle partial flow sampling instrument. Filters were first weighed to the nearest microgram in a temperature and humidity controlled chamber after being allowed to come to steady state conditions within the chamber over the course of 48 hours. Exhaust was diluted with a set proportion of temperature controlled air and passed through these filters. Finally the filters were again allowed to come to steady state for 48 hours after sampling took place and again weighed to the nearest microgram. Trends in brake-specific total PM can be seen in figure 5-9.

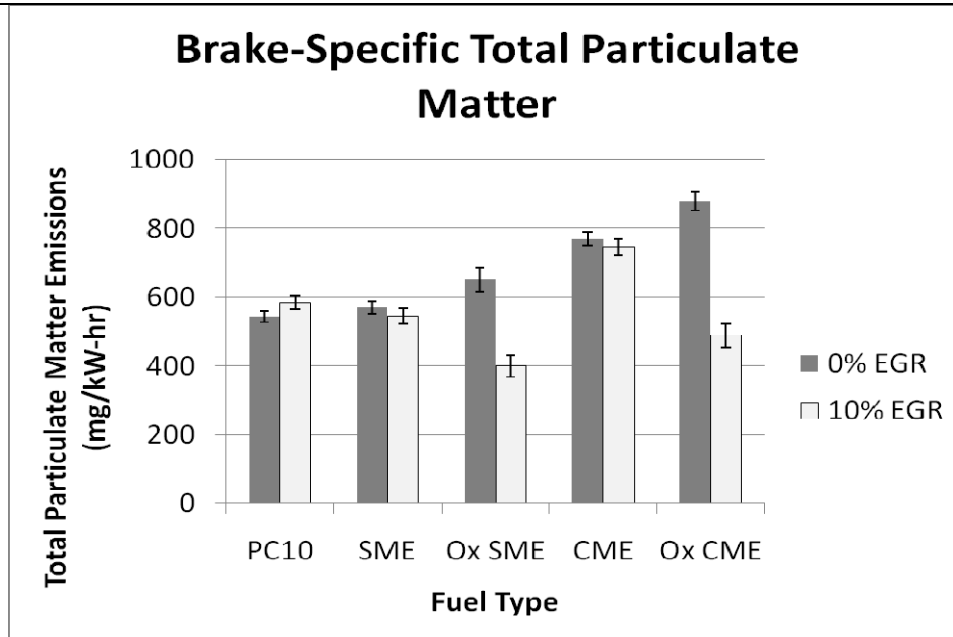


Figure 5-9: Brake-specific total particulate matter emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

The most intriguing trend from this research was the trend in total particulate matter. Contemporary knowledge suggests that lower concentrations of oxygen and peak combustion temperatures cause an overall increase in total PM emissions from the use of EGR by slowing oxidative mechanisms. The Yanmar L70EE research engine showed the expected behavior with ultra low sulfur diesel fuel but showed the opposite behavior when using B20 fuels, decreasing total PM with the addition of EGR. Dramatic reductions of total PM of 39% and 44% were seen when adding EGR to partially oxidized SME and CME respectively. Fresh biodiesel B20 comparatively gave a 3% and 5%

decrease in total particulate matter. To get more detail on possible causes for this trend in total PM emissions, solvent extraction was performed with the results reported in Figures 5-10 and 5-11.

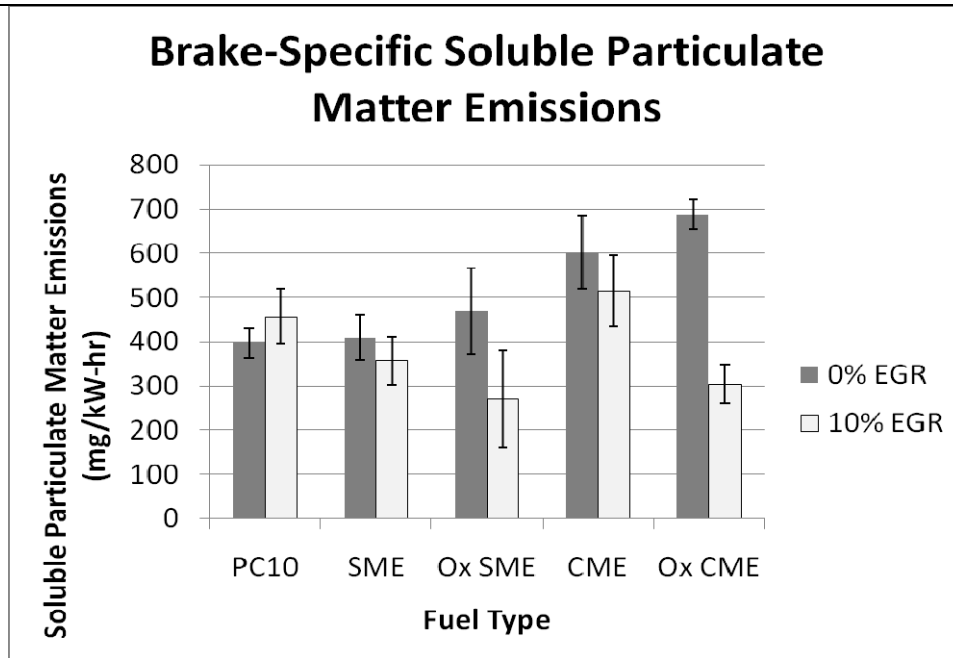


Figure 5-10: Soluble particulate matter emissions with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

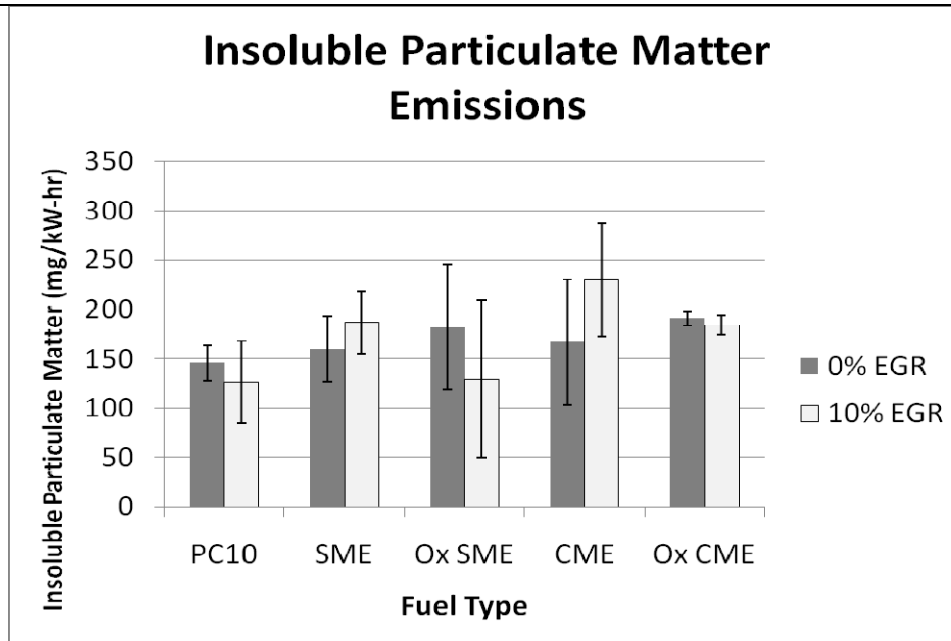


Figure 5-11: Insoluble Particulate Matter with PC10 petroleum diesel and B20 biodiesel blended fuels using soy methyl ester (SME), canola methyl ester (CME), partially oxidized soy methyl ester (Ox SME) and partially oxidized canola methyl ester (Ox CME).

Unfortunately due to the combination of a small particulate matter mass and inherent variation that occurs during soxhlet solvent extraction resulted in high enough variation that few statistically significant trends can be inferred from the data. Results show that without EGR the use of both new and partially oxidized canola methyl ester in B20 blends with ULSD cause an increase in soluble PM. Insoluble PM also increased by about 45 milligrams per kilowatt hour in the case of partially oxidized

CME over the baseline PC-10. When ten percent exhaust gas recirculation was factored in a different trend was observed.

With the addition of EGR there are only two statistically significant changes that take place. Soluble particulate matter decreases by 188 and 153 milligrams per kilowatt hour for partially oxidized SME and CME, respectively, compared to the baseline PC-10 fuel. At the same time, the insoluble particulate matter increases by 103 and 58 milligrams per kilowatt hour for unoxidized and partially oxidized, CME respectively. All of the data indicates that the soluble particulate matter is a much more significant factor in the changes seen in the total particulate matter due to similar trends seen between both soluble and total PM. Unfortunately the error, which comes from the addition of error in total and insoluble PM to be statistically sound, does not allow for most of the trends of soluble PM to be substantiated.

Chapter 6

DISCUSSION

6.1 Summary of Findings

Results of interest in this research include decreases seen in THC and CO emissions both with and without EGR with the use of partially oxidized biodiesel compared to new biodiesel. Slight brake-specific fuel consumption and carbon dioxide emissions advantages were observed with the use of B20 fuel and were even more exaggerated with the use of partially oxidized biodiesel based B20 fuels. Trends in carbon dioxide and fuel consumption were less evident with the incorporation of 10% EGR. In all cases of biodiesel use, both with and without EGR, the “biodiesel NOx effect” was evident. There were statistically significant variations amongst B20 fuel NOx emissions but they were all insignificant compared to the biodiesel NOx effect.

Finally, the most counterintuitive result that requires further analysis was the increase of total particulate matter emissions experienced by all B20 blends compared to the baseline PC-10. These increases in total PM were exaggerated with the use of partially oxidized biodiesel B20 blends without EGR but went on to experience drastic reductions with the use of partially oxidized B20 and 10% EGR. Mentioned above, soluble PM material was seen to be the most likely contributor to the variation in total PM emissions. Unfortunately due to large statistical error caused by the addition of the error from total and insoluble PM measurements, none of the soluble PM changes were significant other than for partially oxidized CME.

6.2 Fuel Injection Timing

Injection timing is often a factor that can change the performance or emissions from direct injection compression ignition engines. Biodiesel is well known to have decreased compressibility (an increased speed of sound) resulting in slightly advanced injection timing for fuels containing large concentrations of biodiesel [22]. Electronic fuel injection systems can avoid this by relying on computer signals that remain fixed to time the start of fuel injection. Figures 6-1 and 6-2 show that with and without EGR both new and partially oxidized CME caused a 0.3° crank angle advance in the start of injection timing.

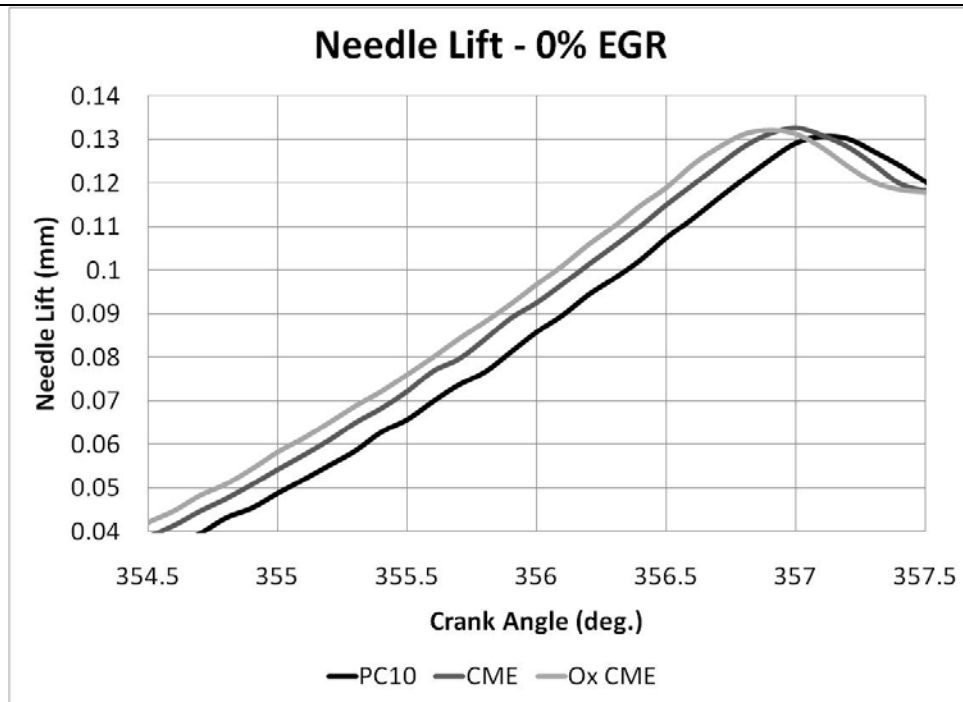


Figure 6-1: Needle lift profile for the fuel injector during 0% EGR trials for baseline ultra-low sulfur petroleum diesel (PC10), canola methyl ester based B20 fuel (CME) and partially oxidized canola methyl ester based B20 fuel (Ox CME). Top dead center occurs at 360 degrees crank angle.

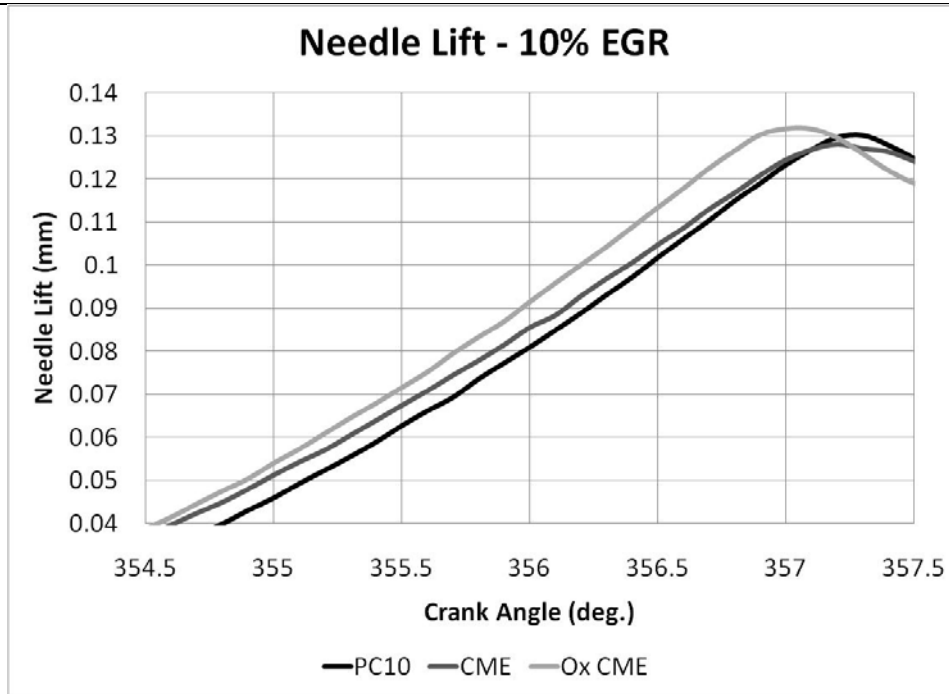


Figure 6-2: Needle lift profile for the fuel injector during 10% EGR trials for baseline ultra-low sulfur petroleum diesel (PC10), canola methyl ester based B20 fuel (CME) and partially oxidized canola methyl ester based B20 fuel (Ox CME). Top dead center occurs at 360 degrees crank angle.

In both figures a fuel injection advance can be seen with the use of all types of B20 compared to PC-10. This helps to explain the elevation of NO_x over the 1% rise in NO_x per 10% biodiesel content in the fuel that is normally expected from the biodiesel NO_x effect. Previous research has also show that even a slight shift in the injection timing that can cause a significant shift in NO_x and PM emissions [36].

6.3 Ignition Timing

Following the injection of fuel there is an ignition delay before the start of combustion in the cylinder. An ignition quality testing (IQT) instrument was used to measure the cetane number of each of the test fuels to give a quantitative figure on the ignition delay expected. Earlier it was seen that the CN increased when each biodiesel was partially oxidized. Figure 6-3 shows the change in ignition delay for PC-10 and both new and partially oxidized SME based B20 through pressure data recorded from the engine. In the previous section it was shown that the start of injection was at approximately the same time so any change in the start of ignition results from the change in the cetane number or other form of fuel chemistry such as EGR.

The twofold attack of EGR on the emissions of NO_x from compression ignition engines also increases the ignition delay with all types of fuel. Radical initiation and propagation is suppressed by the increased specific heat of the incoming air charge with exhaust gas recirculation. Radical initiation and propagation are extremely important to the formation of emissions, especially with the large amount of premixed combustion that occurs in the Yanmar research engine. Figures 6-4, 6-5 and 6-6 all show the effect that EGR had on the ignition delay of PC-10, SME based B20 and partially oxidized SME based B20.

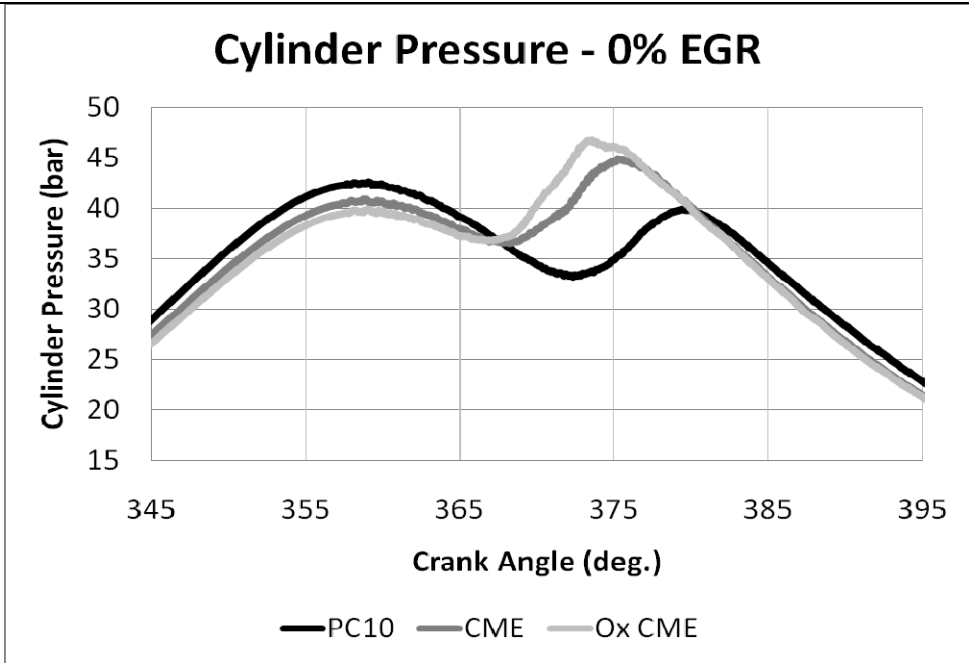


Figure 6-3: In-cylinder pressure trace with 0% EGR and baseline petroleum diesel (PC10), canola methyl ester based B20 (CME) and partially oxidized canola methyl ester based B20 (Ox CME). Top dead center occurs at 360 degrees crank angle.

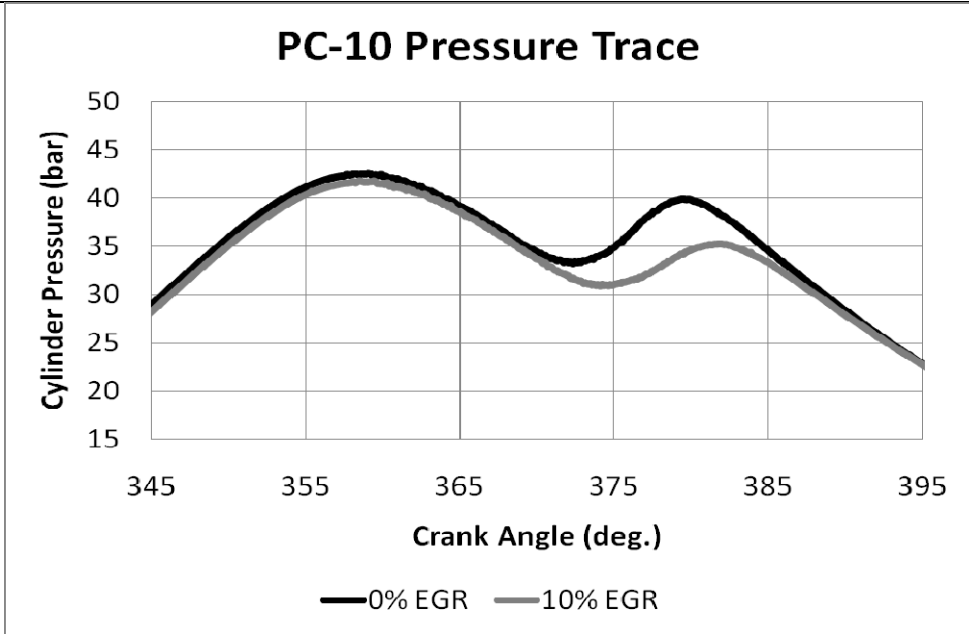


Figure 6-4: In-cylinder pressure trace running on baseline PC-10 ULSD with 0% and 10% EGR

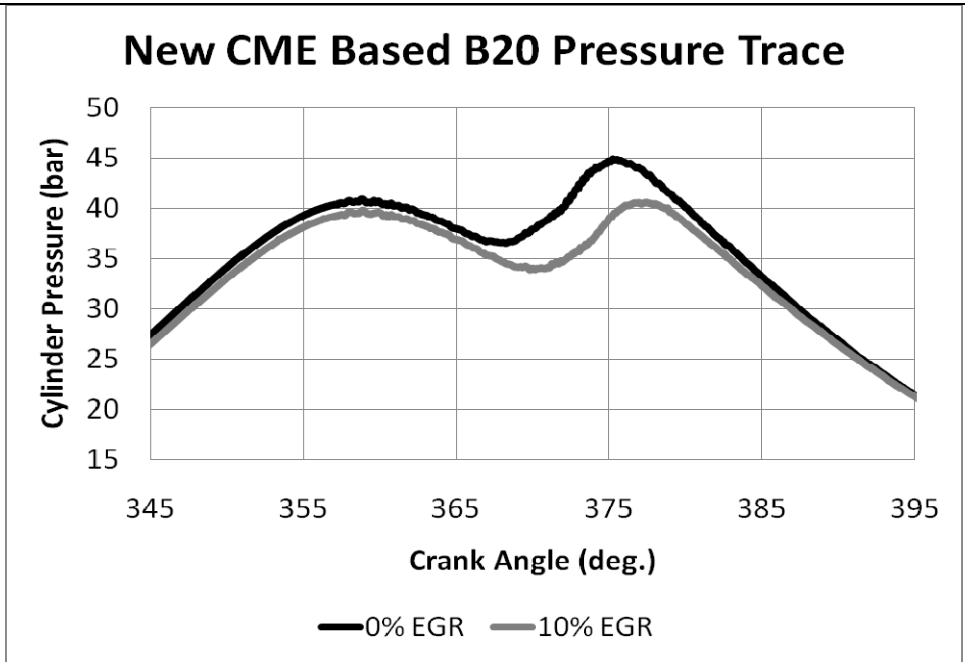


Figure 6-5: In-cylinder pressure trace running on new CME based B20 with 0% and 10% EGR

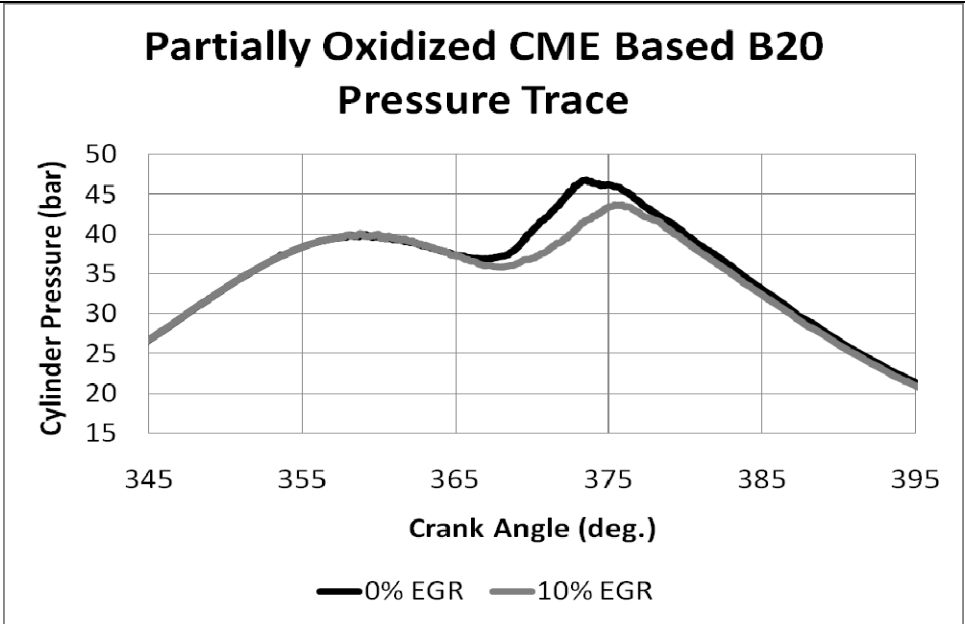


Figure 6-6: In-cylinder pressure trace running on partially oxidized SME based B20 with 0% and 10% EGR

Similar graphs displaying the data for canola methyl ester based B20 fuels can be found in the appendix. In all cases, the pressure can be seen to rise later in the cycle when 10% exhaust gas recirculation was implemented. By advancing the start of combustion through use of biodiesel blends the duration of active combustion has the possibility of being longer. Longer combustion duration gives products of partial combustion a longer chance of being oxidized into final products of combustion such as carbon dioxide. When fuel with a higher concentration of oxygen was added in the form of biodiesel and partially oxidized biodiesel the increased oxygen concentration in the fuel in addition to the longer combustion duration from the ignition advance can decrease the products of partial combustion.

Unfortunately higher oxygen concentrations in the fuel and advancing the ignition closer to top dead center cannot account for the trends seen with unburned hydrocarbons with exhaust gas recirculation and total particulate matter trends both with and without EGR. To get better insight into the observed decrease in THC when adding EGR with B20 fuels along with the unusual total PM trends, analysis of the heat release in the engine must be examined.

6.4 Heat Release

By examining the heat release curves from the Yanmar research engine it was determined to be an “M”-type direct injection diesel engine according to classification found in Heywood [6]. M-type DI engines operate by injecting fuel at a nearly tangential angle to the walls of the combustion bowl in the crown of the piston: earning it the name a “wall-wetting system”. Combustion rate in these engines is limited by the rate of evaporation of fuel from the walls of the piston and mixing of the evaporating fuel with air in the cylinder [6]. Also because of the vast difference of the M-type injection system compared to the more commonly studied multi-hole nozzle DI system, the classic diesel spray diagram cannot be

effectively referenced. Common characteristic shared by both injection systems are the three stages of diesel combustion.

Direct injection compression ignition engines experience three separate combustion phases that all have different effects on emissions [6]. The first of the three phases is the premixed combustion phase. Combustion does not occur at the moment that fuel is injected into the engine but experiences an ignition delay that allows for a significant portion of the diesel to be injected and mixed into an inflammable mixture. When radical formation reaches a critical rate ignition occurs, burning all of the premixed fuel charge, resulting in a relatively short period with a high rate of heat release.

Following the premixed combustion phase there is a period of mixing controlled combustion while fuel is still being injected into the engine while the mixture is actively combusting that can be approximated as a turbulent diffusion flame. During the mixing controlled combustion phase of diesel combustion particulate matter and NO_x formation are the main concerns. The large fuel rich core of the turbulent diffusion flame experiences pyrolysis, forming the polycyclic aromatic hydrocarbons and ultimately diesel particulate matter. Most of the PM is oxidized when it passes through the outer stoichiometric shell of the diffusion flame but some PM remains and is emitted from the engine. NO_x is also a pollutant of interest that forms during the mixing controlled stage in diesel engines. Higher temperatures within the aforementioned stoichiometric outer shell cause thermal NO_x formation to become more favored than at lower temperatures, resulting in high NO_x formation rates. Due to relatively high oxygen concentrations in the exhaust the NO_x cannot be subsequently reduced over a three-way catalysts utilized with spark ignited engines.

Finally the late combustion phase occurs after fuel injection has finished and the remaining fuel rich regions burn to completion. Late stage combustion also results in further oxidation of diesel particulate matter without the simultaneous formation. This means that if one can extend the late stage combustion stage, the brake-specific particulate matter emissions will be reduced. With these factors taken into account, the heat release of the engine was examined for possible sources for the variation in particulate matter emissions. Figure 6-7 and 6-8 shows the comparison between the heat release rate versus the crank angle for PC-10 ULSD, CME based B20 and partially oxidized CME based B20 fuels with 0% and 10% EGR respectively.

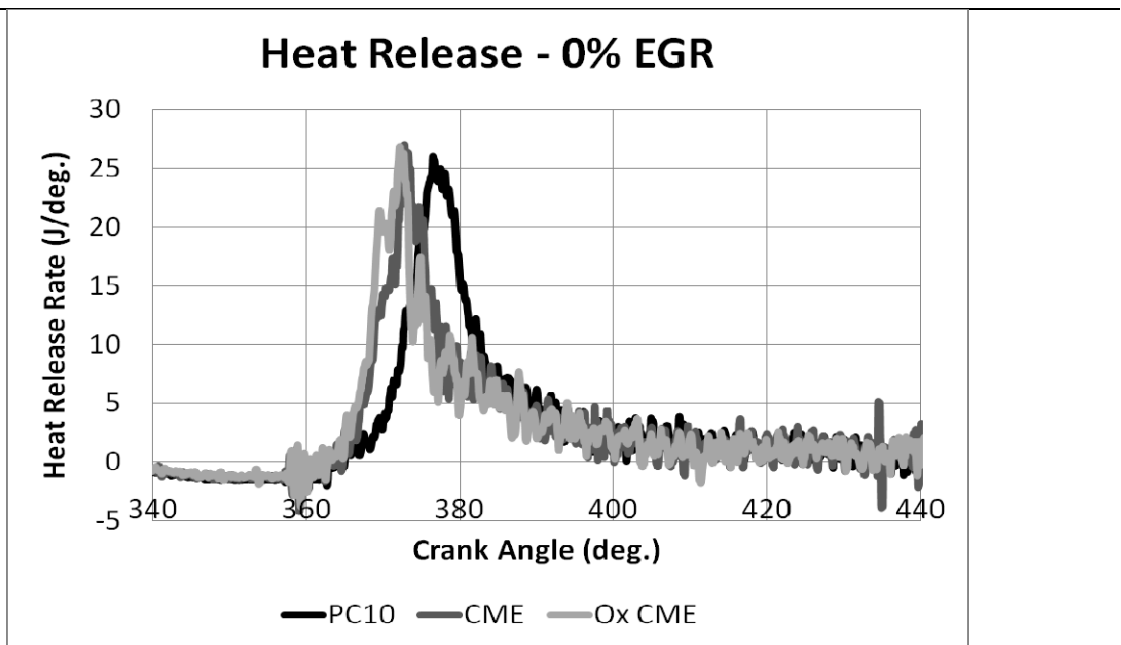


Figure 6-7: Heat release rates for baseline PC-10 and CME and partially oxidized CME based B20 with the use of 0% EGR.

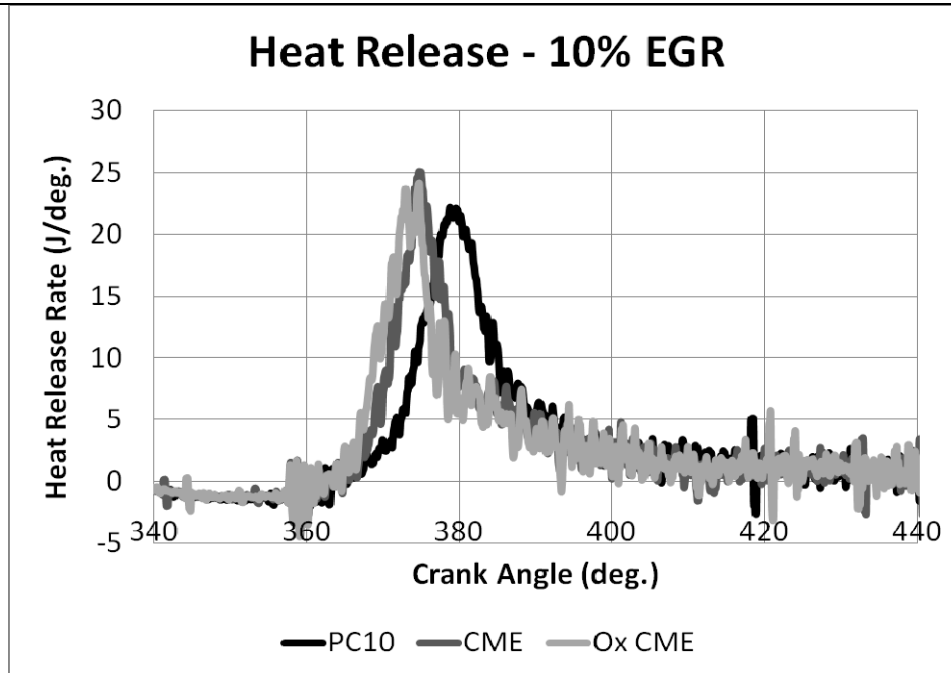


Figure 6-8: Heat release rates for baseline PC-10 and CME and partially oxidized CME based B20 with the use of 10% EGR.

Figure 6-9 and 6-10 show the same curves but they have been standardized to the same crank angle at the start of combustion so that any changes of intensity or duration of any of the three stages of diesel combustion can be seen.

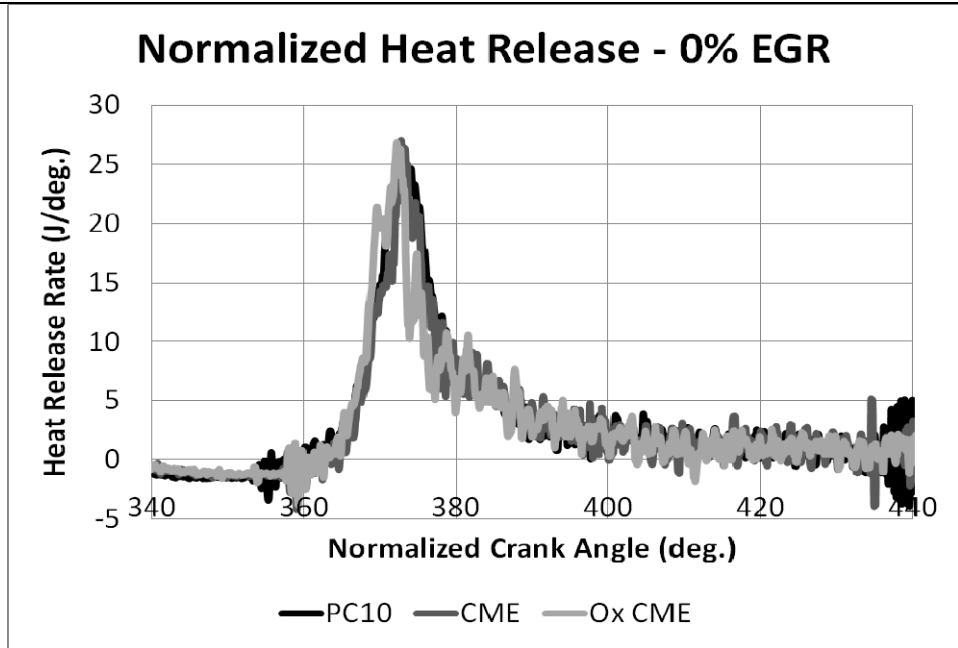


Figure 6-9: Heat release rates for baseline PC-10 and CME and partially oxidized CME based B20 with the use of 0% EGR plotted with a standardized start of ignition.

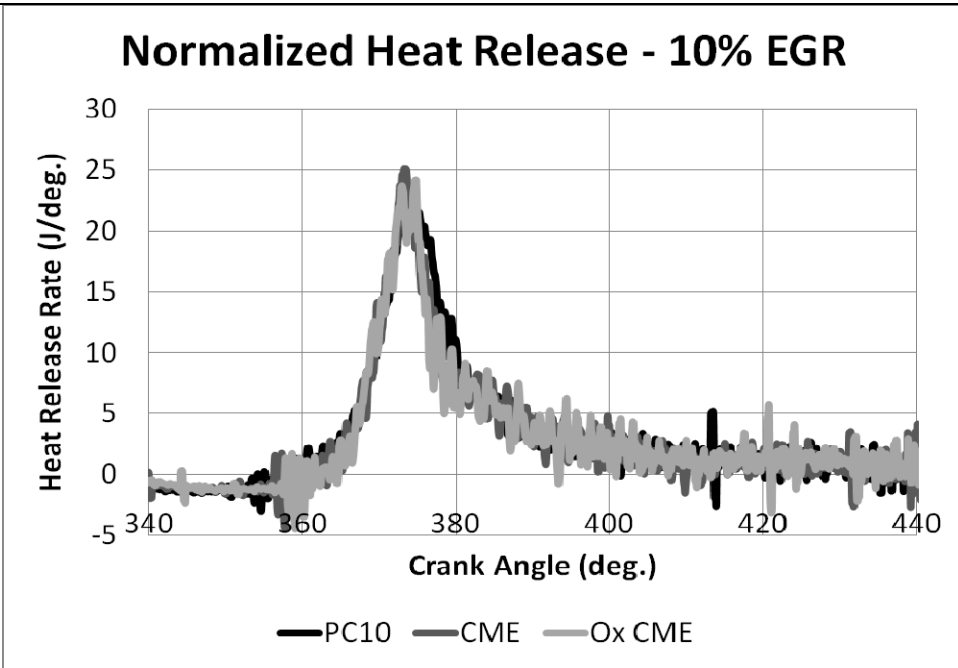


Figure 6-10: Heat release rates for baseline PC-10 and CME and partially oxidized CME based B20 with the use of 0% EGR plotted with a standardized start of ignition.

From the above figures one can see that no significant trends exist when examining the combustion duration. However data in figure 6-7 shows that the peak heat release rate for PC-10 is significantly lower than those of both B20 fuels used when EGR was added. By having a relatively lower peak heat release rate with approximately the same combustion duration compared to both B20 fuels when EGR is added there was a greater amount of fuel left before the late combustion stage began—explaining the change in PM emissions but also why there was a relative increase in THC emissions for this data point. Figures 6-10 through 6-12 show the changes that happen with the heat release when 10% EGR is incorporated compared to without EGR with PC-10 and both CME and partially oxidized CME based B20 fuels.

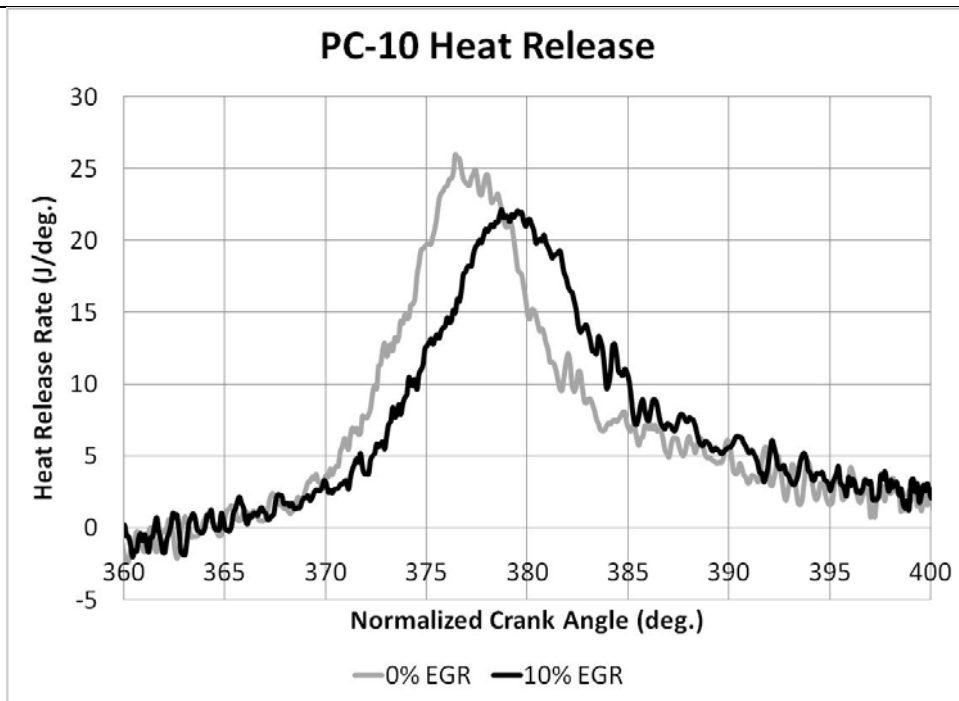


Figure 6-11: PC-10 heat release rates with 0% and 10% EGR

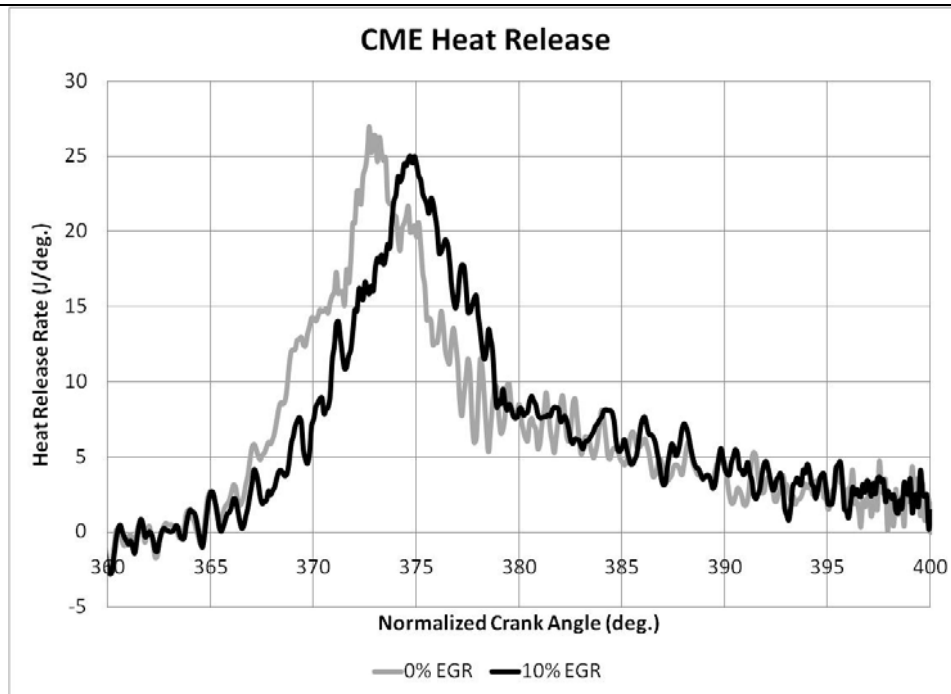


Figure 6-12: CME heat release rates with 0% and 10% EGR

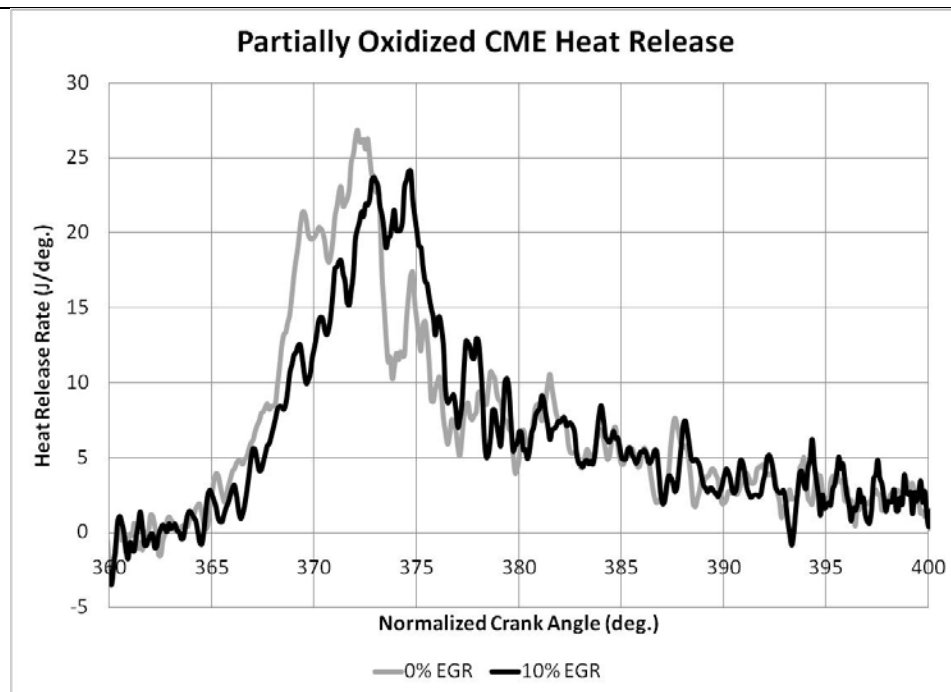


Figure 6-13: Partially oxidized CME heat release rates with 0% and 10% EGR

Single peaks appear in the heat release analysis of all fuels but the partially oxidized biodiesel based B20 fuels. Combustion with a single heat release peak indicated that it was mostly mixing controlled combustion that took place in the cylinder. A second localized heat release peak appeared with partially oxidized biodiesel based B20 indicating a distinct premixed combustion phase that happened before the mixing controlled combustion phase. Without EGR this premixed phase had a much lower than peak heat release rate indicating a relatively small portion of fuel combusting in the premixed phase. However, the addition of EGR delayed the ignition enough to allow more fuel to evaporate and mix with the air. The resulting highest proportion of premixed combustion out of all of the test conditions with partially oxidized biodiesel based B20 and 10% EGR caused the lowest observed total PM levels.

Chapter 7

CONCLUSIONS

7.1 Fuel Property Conclusions

As the oxidation of biodiesel progressed, kinematic viscosity and acid value both increased. Possible reaction pathways leading to these changes suggested in previous research were the formation of polymers, complex organic molecules and volatile acids. Also the derived cetane number of partially oxidized biodiesel was much higher than that of new biodiesel. Reasons suggested in previous research for the decrease in ignition delay associated with the increased cetane number are due to increased concentrations of unstable molecules of fatty acid methyl ester based peroxides.

Gas chromatography mass spectrometry of all of the biodiesel fuel samples did not show any additional compounds formed during the partial oxidation process. However, many of the new compounds that were evidently formed by the observed changes in fuel properties could have been obscured by existing peaks from the original fatty acid methyl esters. Because of that possibility future studies should use two dimensional GCMS to confirm whether or not this is true.

In spite of all of the fuel chemistry changes that resulted from partially oxidizing the biodiesel the fuel stayed within ASTM specifications under all conditions. This means that even the most oxidized biodiesels used in these trials could be used to make commercially acceptable vehicle fuels.

7.2 Engine Emissions

Partially oxidized biodiesel based B20 caused an overall decrease in THC and CO emissions compared to new biodiesel based B20 and baseline PC-10 ULSD. These reductions were also consistent when 10% EGR was added to the intake air charge. Carbon dioxide emissions on the other hand were minimally affected by the use of partially oxidized biodiesel—mainly varying due to a combination of the lower energy density and increased oxygen concentration of biodiesel as well as the observed increase in the cetane number associated with partial oxidation of the biodiesel fuels.

NO_x and particulate emissions showed the most significant trends in this research. As expected the biodiesel NO_x effect was present accounting for a 15% to 22% increase when combined with the observed advance in fuel injection with the use of B20 fuels compared to standard ultra-low sulfur diesel fuel. There was an increase of approximately 4.7% with the use of partially oxidized CME based B20 compared to new CME based B20 when 10% EGR was used but was considered to be minor compared to the effects from biodiesel and EGR use. Finally, when using both partially oxidized biodiesel based B20 fuels with 10% EGR there was a decrease of 20% to 34% in total PM emissions compared to the baseline PC-10 fuel.

These results pointed toward a possible answer to the commonly referenced “NO_x-PM tradeoff” that happens with diesel engines. The NO_x-PM tradeoff references that when running without EGR diesel engines emit relatively small amounts of PM but high in-cylinder temperatures result in high NO_x emissions. By adding EGR and suppressing peak in-cylinder temperatures both Zeldovich mechanisms and PM oxidation mechanisms are slowed down resulting in lower NO_x but higher PM emissions. By

using B20 based on partially oxidized biodiesel EGR can be used to suppress NO_x emissions with a simultaneous PM decrease.

7.3 Combustion Analysis

Pressure trace data allowed for the detailed analysis of combustion characteristics of each fuel under each condition. The first finding was that the heat release fit the classic heat release curve of an “M”-type direct injection engine. Starting with this assumption the standard diesel fuel jet model cannot be used to explain trends seen in data as M-type DI diesel engines wet the walls of the combustion chamber and combustion occurs at rates dictated by fuel evaporation from the piston bowl walls and mixing rates of the evaporated fuel with the surrounding air. Using this as a model the most likely regions where PM and NO_x, the two main emissions of concern from diesel engines, can be expected to form would be just above the wetted wall of the piston bowl and within the stoichiometric flame respectively.

Comparing the heat release rates of all the different fuels with and without EGR became the key comparison to understand the reactions in the engine leading to conditions with simultaneous reductions of NO_x and total diesel particulate matter. When partially oxidized biodiesel was incorporated into the fuel there was much more distinction between the premixed and mixing controlled combustion phases than with pure ultra-low sulfur diesel and B20 fuels based on new biodiesel. Partially oxidized B20 without EGR resulted in a lower than peak heat release rate during the distinct premixed combustion. But, when running with EGR and partially oxidized B20, the premixed combustion phase reaches peak heat release rates. Higher amounts of premixed combustion of a mixture with a higher specific heat in a diesel engine caused the observed simultaneous NO_x and PM

decrease seen when running with 10% EGR and partially oxidized biodiesel based B20. The extra oxygen in the B20 and partially oxidized biodiesel based B20 meanwhile also worked to minimize products of partial combustion by having more oxygen available in the fuel.

Chapter 8

RECOMMENDATION FOR FUTURE WORK

8.1 Fuel Characterization

Detailed characterization pointed toward a change in the composition of biodiesel after 24 hours of oxidation but was unable to pinpoint the exact changes that happened. It was known that volatile acids were formed during the process due to the increasing acid number. However, it was unclear what the exact structure of the acids were but it was very similar to the original methyl ester fuels. A future test to better identify products of partial biodiesel oxidation would be three-dimensional gas chromatography mass spectroscopy. Three dimensional GCMS is a new technology that allows for separation of compounds that appear as a single peak in two dimensional GCMS. From the observed shift in the existing data there were certainly reactions forming new compounds that were just hidden by the FAME peaks that were seen with the new biodiesel sample.

8.2 Engine Testing

Disadvantages of the Yanmar research engine used in this research were the lack of an electronic injection system and the M-type diesel injection system. With an electronic injection system the injection timing can be changed without changing any other parameters of the engine allowing for the correction of ignition timing when working with fuels with varying cetane numbers. By adjusting the ignition to the same crank angle variables such as bulk fluid motion and cylinder temperature can be eliminated assuring that emerging trends from this research remain consistent. M-type diesel engines

are much less studied leading to a lack of knowledge over exact dynamics that happen throughout the engine cycle.

It would make an excellent future research to explore the effects of partially oxidized biodiesel based B20 in a multihole direct injection diesel engine with an electronic injection system at multiple operating conditions. Engine speed and load can have a very large effect on emissions from a diesel engine, therefore it is very important to look at effects of partially oxidized biodiesel based B20 under a variety of engine operating conditions. Electronic multihole fuel injection systems allow for fixing of the start of ignition and introduction of the fuel through a much better studied system for easier analysis of the results. Finally in order to more fully understand the chemical reactions in the engine the PM should be more fully studied coming from the engine.

High resolution transmission electron microscopy (HRTEM) is a common technique of imaging diesel particulate matter. By looking at the grapheme layers within the individual particles, properties of the particulate such as reactivity can be inferred. Knowing properties of the particulate matter would provide even greater in-depth understanding of reactions that take place in the engine. Depending on the perceived reactivity of the particulate matter it would help narrow down the exact mechanism of suppressing PM emissions using partially oxidized biodiesel with EGR—whether it is suppressing PM formation or increasing PM oxidation before being emitted from the engine. After performing all the tests above the kinetics and applicability of partially oxidized biodiesel as an oxygenate additive will be understood enough to recommend or discourage widespread implementation into the on-road fuel supply.

Appendix A

SUPPLEMENTAL DATA

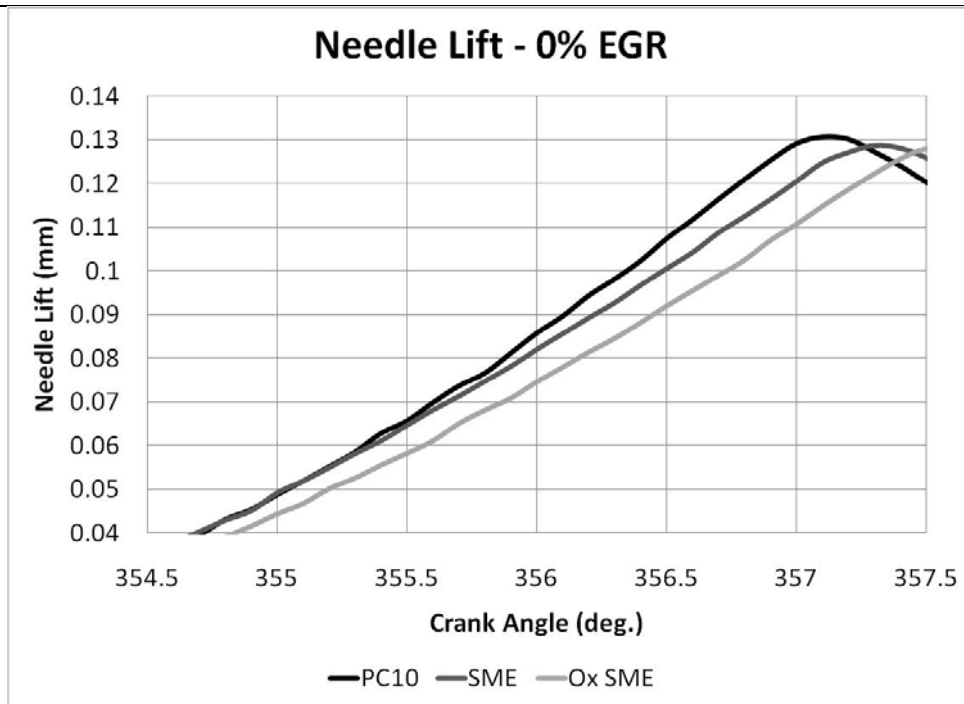


Figure A-1: Needle lift profile for the fuel injector during 0% EGR trials for baseline ultra-low sulfur petroleum diesel (PC10), soy methyl ester based B20 fuel (SME) and partially oxidized soy methyl ester based B20 fuel (Ox SME). Top dead center occurs at 360 degrees crank angle.

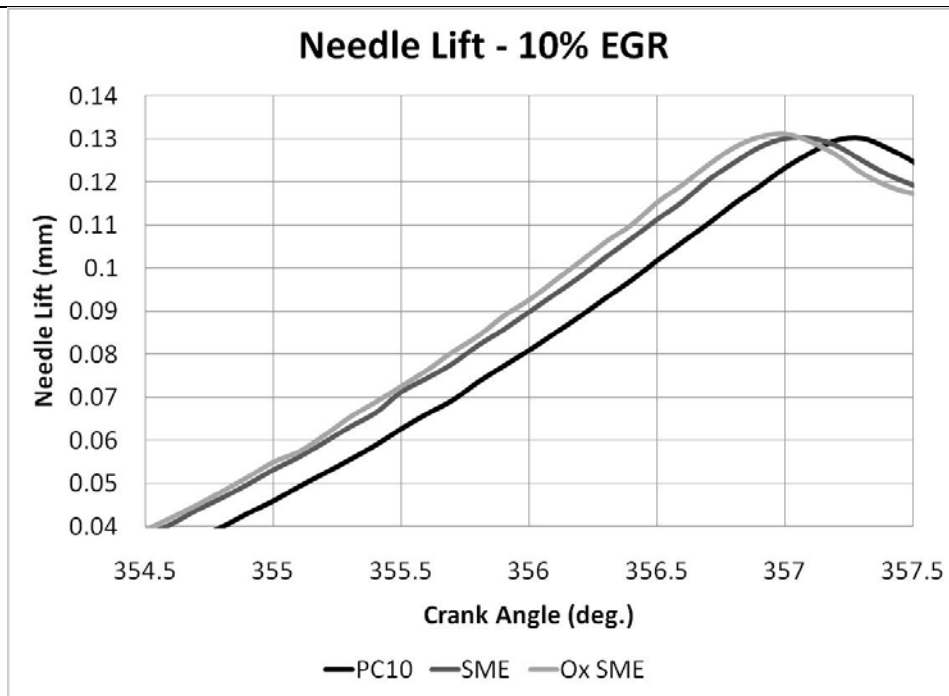


Figure A-2: Needle lift profile for the fuel injector during 10% EGR trials for baseline ultra-low sulfur petroleum diesel (PC10), soy methyl ester based B20 fuel (SME) and partially oxidized soy methyl ester based B20 fuel (Ox SME). Top dead center occurs at 360 degrees crank angle.

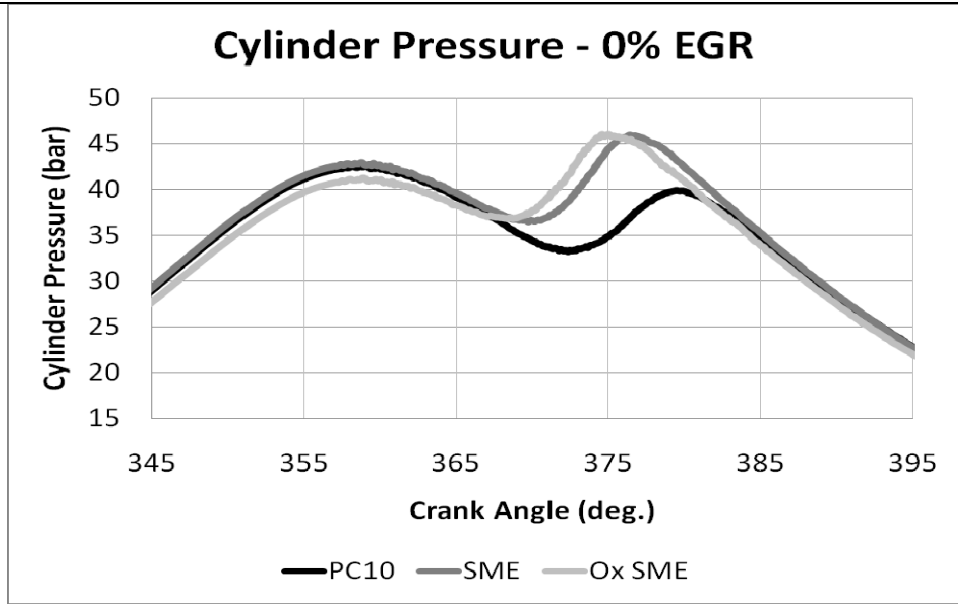


Figure A-3: In-cylinder pressure trace with 0% EGR and baseline petroleum diesel (PC10), soy methyl ester based B20 (SME) or partially oxidized soy methyl ester based B20 (Ox SME). Top dead center occurs at 360 degrees crank angle.

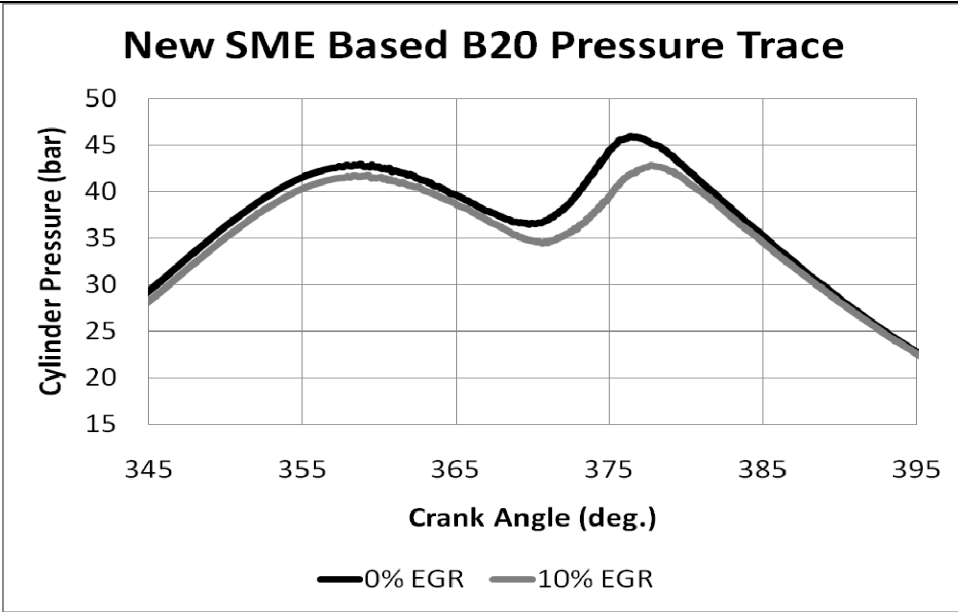


Figure A-4: In-cylinder pressure trace running on new SME based B20 with 0% and 10% EGR

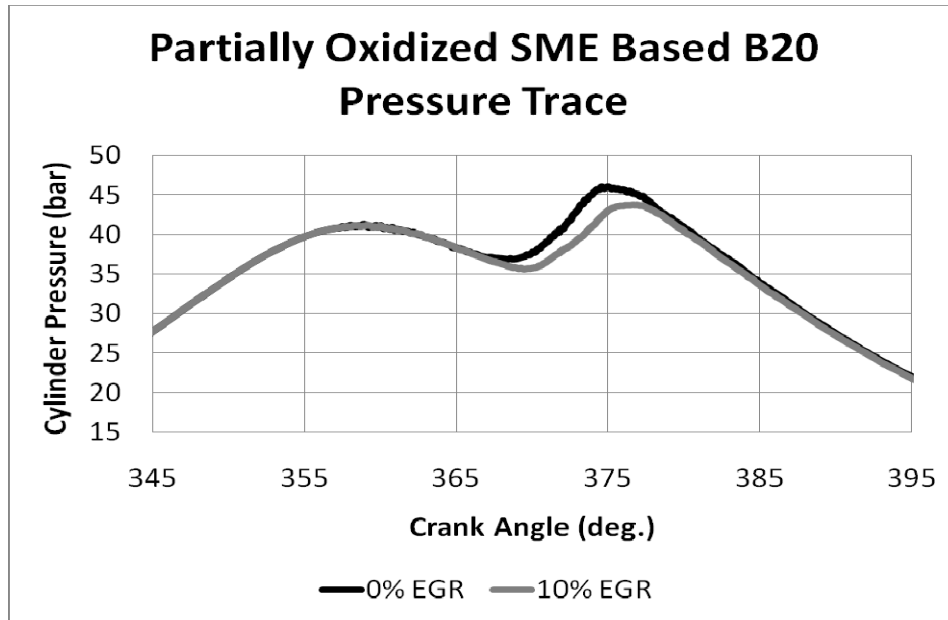


Figure A-5: In-cylinder pressure trace running on partially oxidized SME based B20 with 0% and 10% EGR

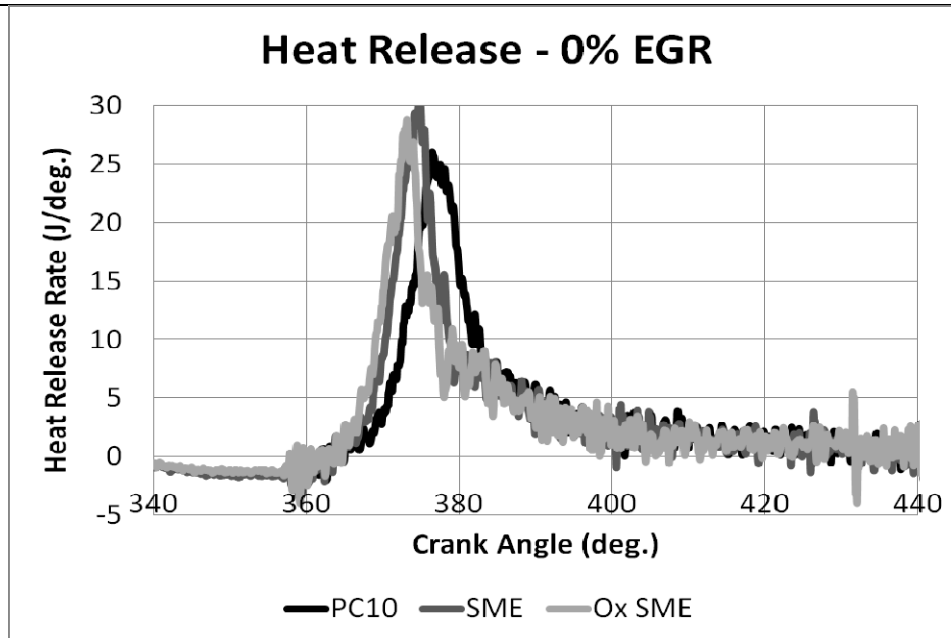


Figure A-6: Heat release rates for baseline PC-10 and SME and partially oxidized SME based B20 with the use of 0% EGR.

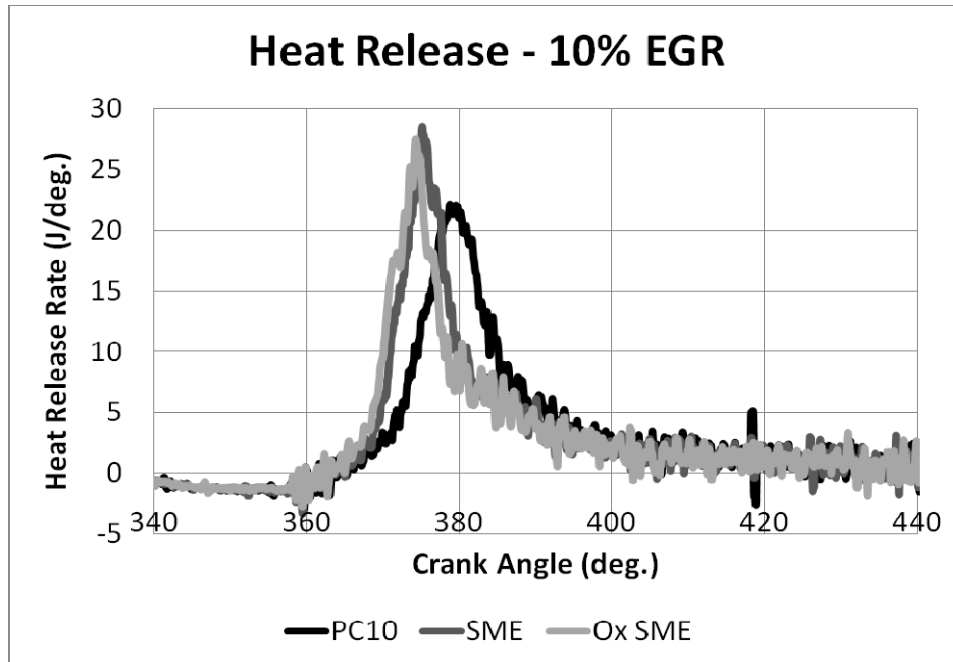


Figure A-7: Heat release rates for baseline PC-10 and SME and partially oxidized SME based B20 with the use of 10% EGR.

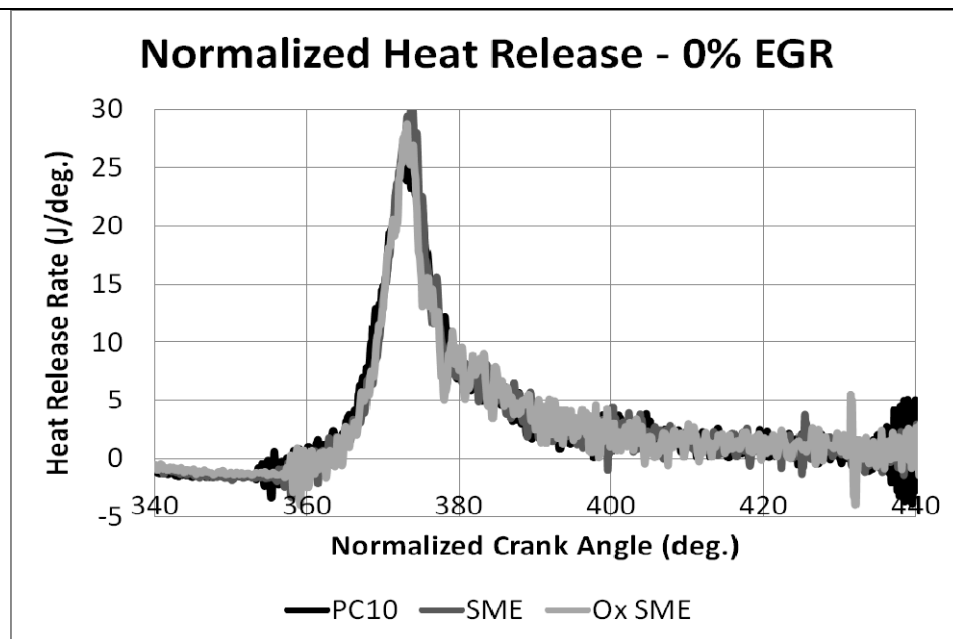


Figure A-8: Heat release rates for baseline PC-10 and SME and partially oxidized SME based B20 with the use of 0% EGR plotted with a standardized start of ignition.

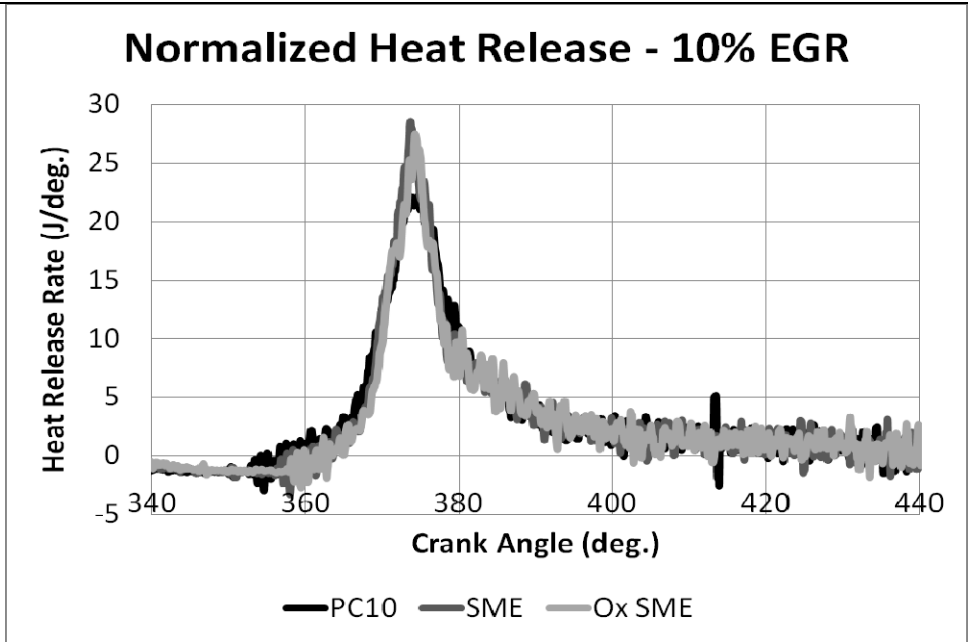


Figure A-9: Heat release rates for baseline PC-10 and SME and partially oxidized SME based B20 with the use of 0% EGR plotted with a standardized start of ignition.

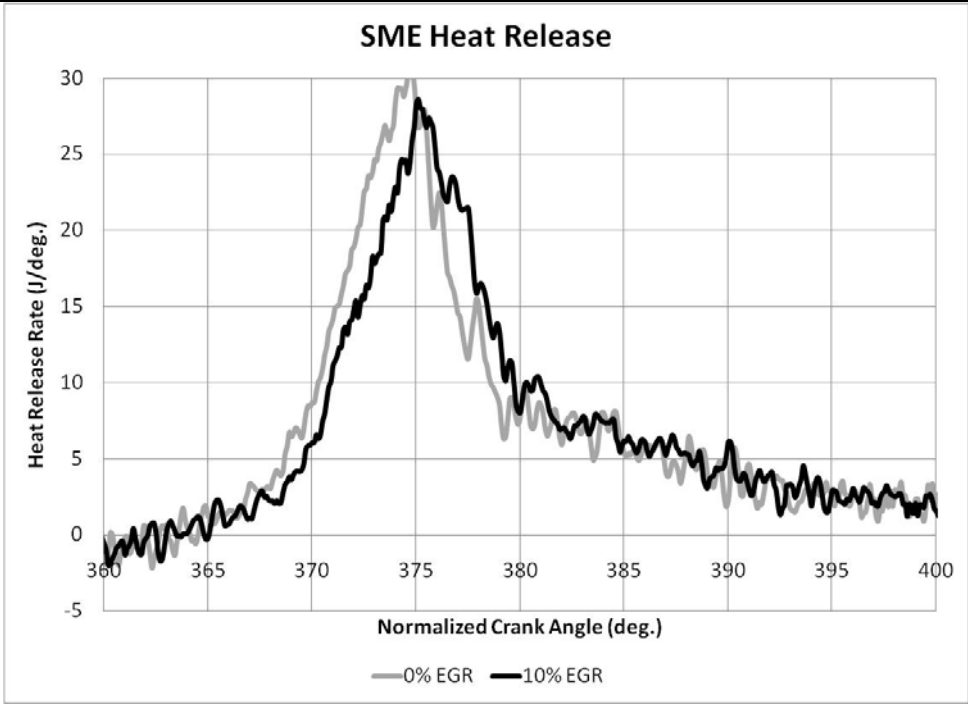


Figure A-10: SME heat release rates with 0% and 10% EGR

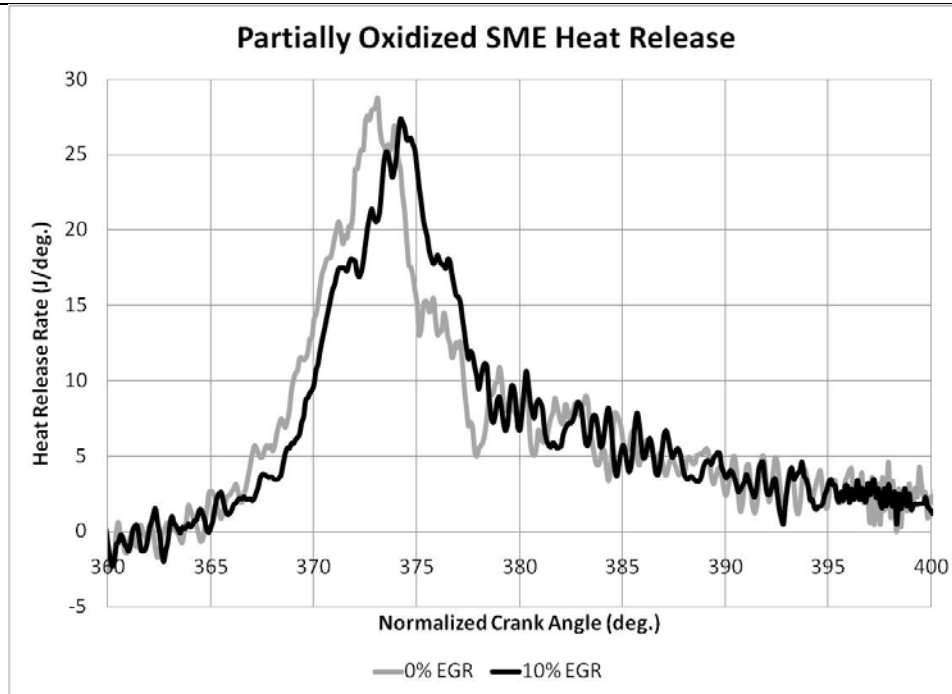


Figure A-11: Partially oxidized SME heat release rates with 0% and 10% EGR

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