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NOx REDUCTION STRATEGIES FOR
COMPRESSION IGNITION ENGINES

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Elana M. Chapman

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The dissertation of Elana M. Chapman was reviewed and approved* by the following:

André L. Boehman  
Professor of Fuel Science and Materials Science and Engineering  
Dissertation Advisor  
Chair of Committee

Alan W. Scaroni  
Professor of Fuel Science  
Associate Dean for Graduate Education and Research, College of Earth and Mineral Sciences

Angela D. Lueking  
Assistant Professor of Energy and Geo-Environmental Engineering

Thomas A. Litzinger  
Professor of Mechanical Engineering

Daniel C. Haworth  
Professor of Mechanical Engineering

Yaw D. Yeboah  
Professor of Energy and Mineral Engineering  
Head, Department of Energy and Mineral Engineering

*Signatures are on file in the Graduate School
ABSTRACT

The scope of this investigation is to explore strategies to reduce NOx emissions from compression ignition engines. Two methods are presented in this collection of studies: 1) NOx reduction accomplished through a change in fuel formulation, specifically through a change in the saturated fuel carbon chains of biodiesel; and 2) NOx reduction accomplished through a mixed mode combustion process utilizing a fumigated fuel and a pilot injection of diesel fuel.

In the first study, a light duty diesel engine was used to investigate the change in saturation of a biodiesel fuel and its impact on NOx emissions. Previous studies have shown that a reduction in the iodine value of a biodiesel fuel produces a reduction in NOx emissions. The iodine value of the fuel is reduced through the saturation of the C18 molecules via hydrogenation of biodiesel fuel. Experiments were performed at several speeds and loads without exhaust gas recirculation (EGR), and a NOx reduction with the hydrogenated diesel fuel was observed. For all the modes studied, the NOx emission was higher for the biodiesel and lower for the hydrogenated biodiesel in comparison to the ultra low sulfur diesel (ULSD) fuel. Results from the calculation of the adiabatic flame temperature shows that the results could be explained by the difference in adiabatic flame temperature of the fuel, thus influencing the prompt NOx contribution in addition to the thermal contribution. Since the adiabatic flame temperatures are similar for the hydrogenated biodiesel and the ULSD, yet the NOx reduction with the hydrogenated biodiesel is much lower than the USLD levels, another explanation for the reduction is suggested: the additional prompt NOx contribution from the change in fuel chemistry.
The second study investigated the NOx reductions which could be achieved with a mixed mode combustion process utilizing a fumigated fuel and a pilot injection of diesel fuel. In this research, the fumigated fuel was dimethyl ether (DME) and DME/Methane blends, while the pilot injection fuel was ULSD. Several sets of experiments were performed to study the ignition of the fumigated fuel, and its impact on the NOx emissions. In the first set of experiments, the DME concentration was spanned over a range of 15 to 44% energy equivalent of the total fuel requirement. An approximately 20% reduction in NOx emissions was observed up to 35% DME energy equivalent. As the energy equivalent increased above 35%, the NOx emissions began to increase with the increase in the peak of the high temperature heat release (HTHR). While the NOx emissions decreased, there was also a significant shift in the NO to NO2 conversion for all DME fumigation test conditions in comparison to the baseline diesel cases. For 25% DME energy equivalent, the injection timing of the pilot diesel was retarded and a reduction in the NOx emissions was observed. The low temperature heat release (LTHR) and the HTHR remained constant in magnitude and timing while the injection timing of the pilot diesel was retarded. The peak pressure for the premixed and diffusion portions merged, with increasing premixed DME combustion. With retarded injection timing, NOx reduction occurred as a result of the decrease in the bulk cylinder temperature and in the combustion duration before cylinder quenching from the exhaust stroke. In the second set of experiments, the intake air temperature was increased to study the impact on NOx and the mixed mode combustion process. While the amount of DME residual in the exhaust decreased along with the total hydrocarbon and CO emissions, the NOx emissions increased with increasing bulk cylinder temperature. For
the speed and load used in this experiment, there was enough fuel and compression to combust most of the fuel, yet not enough to complete the combustion of the unburned hydrocarbons and CO. While air heating shifted the stoichiometry of the fuel and air mixture by reducing the density of air, the heating led to increased NOx with reduction in the NO to NO₂ conversion. This may indicate that the system was above the low temperature range for this conversion to occur. In the third set of experiments, a small amount of Methane was introduced into the system to study the impact on the cetane number of the fumigated fuel. On a brake specific power basis, the Methane addition reduced the NOx emissions more than with only DME, however the NO to NO₂ conversion was lower. NOx emissions were further reduced by retarding the injection timing, but increased with increasing intake air temperature. Through the use of the intake air heating, it was observed that the ignition of the DME/Methane blend was advanced with a smaller LTHR and a higher HTHR. While NOx emissions increased with the increase in bulk cylinder temperature, only the NO emissions increased while NO₂ remained constant. Gaseous emissions analysis showed that the heating caused greater conversion of the Methane and DME during combustion.
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Chapter 1

Introduction

The reduction of oxides of nitrogen emission (NOx) from compression ignition engines is an important objective due to environmental and human health concerns particularly in areas that are ozone non-attainment zones (e.g., Philadelphia, Houston). In addition, NOx emissions from engines and vehicles are legislated and regulated around the world, with the emissions regulations continually tightening in the upcoming years. Thus, many methods that can reduce those emissions from in-use compression ignition engines and vehicles are being considered as options.

There are various methods that can be used to reduce NOx emissions from a compression ignition engine. Two of these methods were studied as a collection of research presented in this thesis. In particular, NOx reductions can be achieved: 1) through a change in the formulation of biodiesel fuel by hydrogenation of the fuel, and 2) through a change in the mode of combustion with the use of a fumigated fuel. Some of these studies have been previously published, and are contained within this thesis in part or in whole.

The first study involves the effect of biodiesel fuel formulation on NOx emissions. Specifically, a NOx increase has been demonstrated widely when using a soy-based biodiesel as a fuel in a compression ignition engine. In the literature, it is suggested that NOx emissions from different types of biodiesel are related to a change in the iodine value of the fuel. The hypothesis of this research is that the reduction in iodine
value of the fuel, which in turn is a change in the saturation of the C18 chain of the fuel, leads to a reduction in NOx emissions. A set of tests were performed in a light duty diesel engine running with its normal fuel injection timing and without EGR over various engine speed and load points. In total, 2 engine speeds and 2 different loads were tested. The normal fuel injection timing includes a pilot injection prior to a main injection.

Based on the preliminary studies, it was expected that the hydrogenated biodiesel would show a reduction in the NOx emissions from this particular engine, but it was unclear what the magnitude would be because the previous work had been completed with the EGR present. This research provides new insight into the impact on exhaust emissions from a change in the chemical composition of the biodiesel fuel while using a pilot and main fuel injection strategy in a light duty diesel engine. It would be beneficial to be able to use an alternative fuel in a diesel engine that would produce less NOx emissions than diesel fuel, which would enhance the motivation to move to non-petroleum sources of fuel.

The second study involved modifying the combustion process by introducing a gaseous fuel into the intake air system. This method is being defined as a “mixed mode” combustion. The engine is allowed to operate in its usual fashion with a diesel fuel pilot injection while another gaseous fuel is being fumigated into the intake air system. For this research, the fumigation fuel was dimethyl ether (DME). The engine was operated at a single speed and load, while the feedrate of the fumigated fuel was varied to study the effect of the fumigated fuel on the combustion process and thus the gaseous emissions. The engine test stand was modified to include an intake air heating system to study the effect of temperature on the ignition behavior of the fuels. The hypothesis of
this research is that a fumigated low ignition temperature fuel can modify the typical
NOx formation paths in diesel combustion and thus reduce the total NOx emissions. The
studies involved several experiments at one specific engine speed and load. First, the
DME concentration in the engine mode was explored to determine the minimum NOx
emissions that could be achieved at a particular single pulse injection timing. In addition,
injection timing was modified at this particular fuel concentration to observe the effect of
combustion timing on the emissions. Next, intake air heating was used to further study
the ignition effect of the DME on the overall combustion process and exhaust emissions.
Finally, a short study was performed to blend Methane into the fumigated DME
concentration and to determine if further NOx reductions could be achieved with this
configuration, and how the ignition behavior of the charge was altered. Based on the
preliminary study, it was expected that there would be some NOx reduction with the
DME fumigated into the engine. The intake air heating is expected to further enhance the
ignition of the DME and demonstrate how an engine configuration could be changed (i.e.
higher compression) to better utilize DME in the engine. While utilization of natural gas
and Methane in a compression ignition engine is highly desired because of its wide
availability, mixing it with DME and testing it in the engine provides insight into the
impact of ignition behavior in reducing the NOx emission in the mixed mode combustion
system, which is presently unclear.
Chapter 2

Literature Review

2.1 Motivation

The motivation for researching NOx reduction strategies stems from several factors. Primarily, governments worldwide, including the United States, are setting new standards for emissions from new compression ignition engines and vehicles. This is being done for the benefit of human health and the environment, via significant reductions of particulate matter and NOx emissions. NOx emissions are the precursors to smog that is produced through photochemical reactions in the atmosphere [1-4]. NO and NO$_2$ also readily dissolve into water, and thus form nitric acid, the major contributor to acid rain [4]. In a report to the World Health Organization, the health effects of diesel particulate matter emissions exposure were reviewed and shown through epidemiological studies to give higher incidences of cancer in animals, as well as higher incidence of lung cancer in people who experience high concentrations of diesel exhaust [5].

The target for accepted NOx emissions in the US has been tightened over the last 25 years by the U.S. Environmental Protection Agency (EPA). Between 1997 and 2000, the EPA set new Federal emission standards for on-road diesel vehicles that dramatically reduced allowable nitrogen oxide (NOx) and particulate matter (PM) emissions. Under these new standards, model year 2004 (MY2004) NOx emissions from on-road heavy-duty diesel engines were half those required under MY1998 standards (2.5 g/KW-hr in
MY2004). Starting with MY2007, new on-road heavy-duty diesel engines needed to achieve PM levels and phased-in NOx (starting from 2007, ending in 2010) that are only 10% of MY2004 levels [6]. As a result, diesel engine and vehicle manufacturers needed to implement exhaust after-treatment control devices to meet the MY2007 and later (MY2007+) requirements. These standards were implemented in conjunction with Federal ultra-low-sulfur diesel (<15-ppm sulfur) production requirements, facilitating the introduction of low-emission technologies that would otherwise be compromised by high sulfur levels in the diesel engine exhaust. Figure 2.1 and Figure 2.2 show a historical perspective of the regulations for diesel engines in Europe and the US. Table 2.1 shows the current challenging state of US emissions regulations for Heavy-Duty Diesel Engines.

Figure 2.1: United States and European Union PM Regulations [7]
In addition to the health effects issues, the US is focused on integrating fuels from non-petroleum feedstocks into the fuel inventory for US commercial and consumer use.

Some of the fuels being considered have been shown to increase certain emissions that
are under regulatory control. The introduction of these alternative fuels into the inventory is of great importance to the US economy and security, and thus research and development to minimize the exhaust emissions is required.

However, what is not clear is how to meet these regulations with diesel and alternative fuels. Researchers are pursuing many options, including pre-combustion, in-cylinder and post combustion technologies, and combinations of each. To meet 2007 particulate matter emissions regulations, diesel engine manufacturers are pursuing exhaust after-treatment devices since the technology is available. To meet 2010 emissions regulations, researchers are focusing on exhaust after-treatment devices and in-cylinder methods of emissions control, including homogeneous charge compression ignition engines and other low temperature combustion strategies. The research proposed includes a combination of these options to meet the aggressive NOx emissions reductions: exhaust after treatment technologies, modifying the chemical properties of the compression ignition fuel, and induction of a mixture of fuel and air into a compression ignition engine while using a diesel fuel pilot to ignite the fuel-air mixture.

2.2 Compression Ignition Engines and the Autoignition Process

The words “compression ignition” refer to the engine classification based on the method of fuel ignition. The compression ignition (CI) process is used in conventional diesel engines by pilot injection of diesel fuel. In this type of engine, air is inducted into the cylinder, and compressed. Just before the combustion process is to start, the fuel is injected into the engine. For a given engine speed, the air flow is essentially constant,
and engine load can be adjusted by increasing the amount of fuel injected for each cycle.
There are several variations on the type of CI engine including the working cycle (2 or 4
stroke), method of air preparation (naturally aspirated or turbocharged), and method of
fueling (indirect or direct injection) [11].

The compression of the fuel and air mixture causes the mixture to autoignite. As
Heywood describes it, autoignition is defined as a rapid combustion reaction which is not
initiated by an external ignition source [11]. In the literature about basic combustion
research, this kind of autoignition is described as an explosion. However, to the engine
combustion researcher, the term autoignition is preferred over thermal explosion [11].

A fuel’s autoignition tendency is described by its cetane number. Compression
ignition engines require a fuel to have a cetane number of at least 40 or higher. Normal
ULSD (Ultra Low Sulfur Diesel) has a cetane number of around 50, according to fuel
certificate of analysis.

The autoignition of the fuel and air is a complex reacting system where the
chemical mechanisms consist of a large number of simultaneous and interdependent
reactions or chain reactions [11]. It occurs when the energy being released by the
reacting system overcomes the required heat loss to the surroundings. Modern
autoignition combustion is described through the use of the chain reaction processes:
initiating reactions, propagation reactions, and termination reactions. There are some
propagating reactions that produce two radical molecules for each radical that is
consumed in the reaction, referred to as a chain branching reaction. When the chain
branching reactions occur very rapidly, the term chain branching explosion is used to
describe the system [11, 12]. Pfahl and coworkers have described the self-ignition
behavior of diesel-relevant fuels in a homogeneous mixture to have a two-step self
ignition, with the first step considered a cool flame, followed by a deflagrative phase
(negative temperature coefficient), then by a secondary explosion [13].

The compression ignition combustion process is typically described as having
three main phases: 1) ignition delay, 2) premixed or kinetically controlled combustion,
and 3) diffusion, or mixing controlled combustion. First, after the fuel is injected, there
is some ignition delay as the fuel and air mix together, the fuel droplets are vaporized,
and a combustible mixture is created. The ignition delay period ends when autoignition
occurs. Second, upon autoignition, a premixed phase of combustion occurs where the
fuel and air that are mixed during the ignition delay period are consumed. This results in
a high rate of pressure rise and heat release. Finally, the diffusion phase of combustion
occurs. During this phase, a diffusion flame front surrounds the fuel spray. At the flame
front, stoichiometric mixtures of the fuel and air are present. The rate of reactions and thus
the rate of heat release are controlled by the rate of mixing of the fuel and air. Figure 2.3
shows an example of a heat release diagram and each of these three phases represented
2.2.1 Low Temperature Heat Release

Low temperature heat release has been shown to occur during the first stage of ignition in the low temperature chemical kinetic reactions of the hydrocarbon oxidation [14]. Higgins and coworkers observed a two stage ignition process while running a heavy duty diesel engine at moderate load [14]. The low temperature chemistry exhibited a slow rise in pressure and is shown in the chemiluminescence of the spray [14]. Earlier work by Dec and Espey also showed evidence of the pre-ignition cool flame characteristics [15].

The low temperature reactions would occur below approximately 760K, which is the temperature at which there is a decrease in the reactivity of the system, labeled as
NTC (negative temperature coefficient) behavior and demonstrated by Curran and coworkers as being caused by the competition between two decomposition pathways that provide lower reactivity [16, 17]. Curran and coworkers elucidated the reaction mechanisms for n-heptane and iso-octane ignition, and thus differentiated the low temperature and high temperature regions and their reaction steps[16, 18].

Flynn and coworkers showed that the first stage ignition can cause an increase in the temperature of the reaction zone by 200-300 °C [19]. However, the magnitude of this behavior is dependent on the fuel properties and whether the fuel exhibits some low temperature heat release [20].

Of interest to the present research are the low temperature reactions and heat release of dimethyl ether (CH₃OCH₃). Through the early research on the chemical kinetics of DME oxidation, it has been demonstrated that the radical reactions during the propagation phase of the combustion process of dimethyl ether include OH, H and CH₃ [21]. With the presence of the OH radical, the ignition quality is enhanced by making the fuel mixture more reactive, thereby shortening the ignition delay and increasing oxidation rates. When the OH radical was present and DME was provided, the reaction continued. The proposed reaction channels for the presence of the OH radical are given in Eq. 2.1 and Eq. 2.2 [22]:

\[
\text{CH₃OCH₂ + O₂ + M } \rightarrow \text{CH₃OCH₂O₂ + M} \quad 2.1
\]

\[
\text{CH₃OCH₂ + O₂ } \rightarrow \text{2 CH₂O + OH} \quad 2.2
\]
From other work, the proposed decomposition reactions include the following chain reaction in Eq. 2.3 [21]:

$$\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3 + \text{CH}_3\text{O}$$  

Then, a CH$_3$ radical abstracts a hydrogen atom from a second molecule of dimethyl ether by the reaction Eq. 2.4:

$$\text{CH}_3 + \text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{CH}_2\text{OCH}_3$$  

The resulting CH$_2$OCH$_3$ radical then decomposes to formaldehyde and methyl radical, and then finally to formaldehyde and Methane, according to the following reactions Eq. 2.5 and Eq. 2.6 [21]:

$$\text{CH}_2\text{OCH}_3 + M \rightarrow \text{CH}_3 + \text{CH}_2\text{O} + M$$  

$$\text{CH}_2\text{OCH}_3 + M \rightarrow \text{CH}_4 + \text{CH}_2\text{O} + M$$  

Within this study, the author proposed and concluded the following competitive reactions through an ab initio calculation, given in Eq. 2.7:

$$\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_3\text{O} + \text{CH}_3$$  

$$\rightarrow \text{CH}_3\text{OCH}_3 + \text{H}$$  

$$\rightarrow \text{CH}_4 + \text{CH}_2\text{O}$$  

$$\rightarrow \text{CH}_3\text{OH} + \text{CH}_2$$  

$$\rightarrow \text{CH}_3\text{OCH} + \text{H}_2$$
A focus on experiments to confirm portions and proposed mechanisms of DME kinetics in the low, intermediate and high temperature regions has yielded a better understanding of the oxidation mechanisms [23-25]. A schematic presentation of those mechanisms is shown in Figure 2.4 [24]. At low temperatures, the methoxymethyl radical (CH$_3$OCH$_2$) adds to molecular oxygen and forms the methoxymethyl-peroxy radical (CH$_3$OCH$_2$O$_2$) [24]. After an intramolecular H isomerization, this radical proceeds through a reaction scheme shown in Figure 2.4. In the ranges of temperatures from 550-600 K, chain branching is due to the reaction pathway leading through the carbonyl-hydroperoxide (HO$_2$CH$_2$OCHO) with the formation of two hydroxyl radicals. As the temperature increases above 600 K, the beta (β) scission of the hydroperoxy-methoxymethyl radical (CH$_2$OCH$_2$O$_2$H) increases [24]. This path produces one hydroxyl radical and 2 molecules of formaldehyde, decreasing the reactivity of the system and leading to the NTC region between 600-725K. When the temperature reaches above 730 K, the hydrogen peroxide (H$_2$O$_2$) dissociates into two hydroxyl radicals leading to the rapid consumption of the rest of the DME fuel [24].
Dagaut and coworkers performed experimental and detailed kinetic modeling studies of the low temperature oxidation of DME with NO to determine the sensitivity of the reactions of DME in the presence of NO [26]. It was shown that above 600K, NO enhanced the oxidation of DME and yielded methyl formate, and the NO was oxidized to NO₂ [26]. Below the 600K, the oxidation of DME was inhibited by the NO [26]. They
present a detailed chemical kinetic mechanism and go on to explain the reactions that inhibit DME oxidation below 600K [26].

Pfahl and coworkers’ research confirmed that DME exhibits the typical two stage heat release characteristic of some hydrocarbons, that has since been shown in research from Dec and Flynn [13].

2.3 Diesel Emissions

The previously described combustion process results in some emissions that are undesirable. Diesel engines have been traditionally high emitters of NOx and particulate emissions. Other pollutants include carbon monoxide (CO) and unburned hydrocarbons (HC). These are typically very low for a diesel engine since the air–fuel mixture is lean of stoichiometric [11, 27]. The following sections will focus on the two major pollutants from a diesel engine, NOx and particulate matter.

2.3.1 Diesel Combustion Conceptual Model

Several researchers have developed and expanded on the conceptual model of diesel combustion [28, 29]. Figure 2.5 shows the most currently accepted model for the diesel fuel spray and flame developed from laser-based measurements [29]. As the liquid fuel leaves the nozzle and travels out as a jet, it rapidly entrains hot air in the cylinder thus initiating fuel vaporization [19]. This leads to the formation of a boundary of fuel-vapor and air mixture in the shear layer along the sides of the fuel jet. The beginning part
of the fuel oxidation process takes place as the fuel-vapor and air mixture enters the jet.

The final oxidation process takes place around the edges of the jet. Figure 2.5 shows this 2 stage fuel oxidation process. The region of this fuel-vapor and air mixture can have an equivalence ratio from 2-4. In Dec’s research, the NOx emissions are produced in the thin layer around the diffusion burning interface. This interface is identified by a thin layer of OH fluorescence [19].

Figure 2.5: Schematic of the conceptual model of DI diesel Combustion [29]

Figure 2.6 provides additional detail on the thermal and chemical variations inside the burning fuel spray plume. Cold liquid fuel enters the warm air supplying the reactants of a rich premixed zone that feeds the interior of the plume. The rich combustion products are oxidized at the surface of the diffusion flame. It is believed that no free oxygen is available inside the diffusion flame layer. The diffusion flame layer has the constituents and temperature for the formation of diesel particulate [19].
2.3.2 NOx Emissions

Oxides of nitrogen (NOx) are formed as a result of the combustion process. NOx includes NO and NO₂. Diesel engines produce significant amounts of NOx, depending on the load conditions of the engine. Of the 100 to 2000 ppm which is produced, the majority of this (greater than 80%) is nitric oxide (NO), with the balance being NO₂ [11]. There are several mechanisms for the formation of NOx: Fuel NO, Thermal NO, Prompt NO, and NO₂.
Fuel NO comes from the oxidation of fuel-bound nitrogen to an oxide of nitrogen. However, the fuels used in this research have little or no fuel bound nitrogen. While the initial fuel bound nitrogen is not present, there are fuel radical-bound nitrogen reactions that play a role in the formation of NO. Those postulated reactions, also typically called the fuel reburn reactions, are shown in Figure 2.7 and act in the same manner as the prompt NO mechanisms.

The amount of prompt NO typically is considerably smaller than the amount formed by the thermal NO mechanism. The prompt NO mechanism (or sometimes called the Fenimore mechanism) occurs as a result of hydrocarbon species (CH or C₂) and atmospheric nitrogen in the flame zone and occurs very rapidly [30]. Their reaction in the flame zone could make nitrogen available for oxidation in addition to CN and HCN, and thus leads to NO production. The Fenimore reactions that are the main focus are shown in Eq. 2.8 and Eq. 2.9, where Eq. 2.8 is the primary reaction and rate limiting [31, 32].

\[
\text{CH} + \text{N}_2 \rightarrow \text{HCN} + \text{N} \quad 2.8
\]

\[
\text{C} + \text{N}_2 \rightarrow \text{CN} + \text{N} \quad 2.9
\]

When the equivalence ratio is less than 1.2, the reactions proceed from hydrogen cyanide (HCN) according to the following chain sequence Eq. 2.10, Eq. 2.11, Eq. 2.12 and Eq. 2.13 [31]:

\[
\text{HCN} + \text{O} \rightarrow \text{NCO} + \text{H} \quad 2.10
\]
Eq. 2.13 is also a reaction involved in the thermal NO mechanism, as well.

The main reactions for zones where the equivalence ratio is above 1.2 are shown in Figure 2.7, where the NO is recycled to HCN in a slower reaction scheme and where NO is actually destroyed [31-33].

In the case of the diesel engine, the most significant mechanism is the extended Zeldovich mechanism, also known as the thermal NO mechanism in which NO is typically found and formed in the post flame zone at a slower rate than the prompt NO.
The extended Zeldovich mechanism consists of the following three reactions, Eq. 2.14, Eq. 2.15, and Eq. 2.16:

\[ \text{O + N}_2 \rightarrow \text{NO + N} \]  
\[ 2.14 \]

\[ \text{N + O}_2 \rightarrow \text{NO + O} \]  
\[ 2.15 \]

\[ \text{N + OH} \rightarrow \text{NO + H} \]  
\[ 2.16 \]

NO formation is strongly dependent on temperature [11]. It is typically formed during the first 20 degrees of crank angle, after the start of combustion. Therefore, emission reduction strategies target this time period, and aim to reduce the combustion temperatures [34].

NOx also includes NO\textsubscript{2} emissions. Glassman discusses briefly the literature on contributions to NO\textsubscript{2} emissions reported in exhaust gases and in flames [12]. He notes that these results seem surprising since kinetic models have indicated that NO\textsubscript{2} formation and reduction can be neglected in practical devices. Merryman and Levy examined NOx formation in a flat flame burner operated near stoichiometric conditions [35]. They postulated a series of reactions that represent their findings, shown below in Eq. 2.17, Eq. 2.18, and Eq. 2.19:

\[ \text{HN} + \text{O}_2 \rightarrow \text{NO} + \ldots \]  
\[ 2.17 \]
In the low temperature regions of the visible flames, they measured large concentrations of HO2 that can react with the NO in the high temperature regions and diffuse back to the lower temperature regions of the flame [35]. They also found that NO2 is consumed rapidly in the near post flame zone, where the NO concentration also rose. The significant reaction is represented by Eq. 2.18 [35]. Glassman suggests that the NO2 formation is further supported by the fact that Eq. 2.18 is two orders of magnitude faster than Eq. 2.19 [12]. Cernansky and Sawyer also concluded from their experiments with turbulent diffusion flames that the high levels of NO2 were a result of the HO2 reaction with NO and O atoms [36]. Hilliard and Wheeler also showed the presence of NO2 in engine exhaust [37].

More recent research has focused on the hydrocarbons in the turbulent diffusion flame [38-41]. Hori has investigated low concentrations of various hydrocarbons below C4H10 and their effect on NO2 conversion between 600 K and 1100 K. Meunier and coworkers focused on the formation and destruction of NO in a propane diffusion flame. They showed that the prompt NOx mechanism was a dominant route, in addition to the reactions between NO and hydrocarbon radicals such as HCN in what is typically described as fuel reburn. Cheng, Mueller and coworkers have also shown the increase in NO2 emissions with the decrease in NO emissions in a dilute mixing controlled combustion in an optical direct injection diesel engine [42-44].
2.3.3 Particulate Matter Emissions

Particulate matter can be defined as the combination of soot, condensed hydrocarbons, sulfates, oil, and water that attach to agglomerated soot particles in the exhaust stream [45]. Soot formation takes place in an environment in the engine that is 1000 to 2800 K and at pressures from 50 to 100 atmospheres [11]. Particulate matter can also be divided into two separate groups, the soluble and the insoluble fraction [46]. The insoluble fraction is comprised mainly of the elemental carbon formed in the diffusion flame that agglomerates into soot. The soluble portion of the particulate matter emissions are the hydrocarbon species that condense and adsorb on the insoluble portion. The aerosol of solid phase particles in the exhaust gas are further described by the total amount of the condensed phase per unit volume of the exhaust gas, and the number of soot particles per unit volume with a specific size diameter characteristic range of the total group [11]. For particle sizing, the particles are typically assumed to be spherical, while TEM photos show that this is not the case. Figure 2.8 is a representation of the various types of compounds present in particulate matter emissions.
Detailed modeling and experiments have been conducted to try to understand the soot formation process in different types of flame structures and in flames of various fuels [47]. It has been established that several classes of hydrocarbons, namely polycyclic aromatic hydrocarbons (PAH) and acetylene (C₂H₂), are important precursors to soot formation and are created in fuel-rich conditions [11, 48]. From the initial formation of a benzene ring, the soot particle increases in size through the addition of acetylene [48]. The adsorption and condensation of the hydrocarbons occurs after the soot leaves the cylinder and begins to cool in the exhaust gas stream [11].

2.4 Emissions Reduction Strategies

Emission control strategies can be divided into three categories: pre-combustion, in-cylinder, and post-combustion [49, 50]. A list of common approaches for each area can be found below in Figure 2.9 [49]. For many years, diesel engines have escaped the
necessity of post-combustion controls because of modifications which could be made to fuel or to the engine to meet any new set of emissions regulations. However, an important requirement for implementation of many post-combustion technologies is the reduction of the sulfur content of the fuel, i.e., the pre-combustion area. This was just accomplished with the introduction of the ultra low sulfur diesel fuel (ULSD) in October of 2006 mandated by the EPA [8, 10]. The following discussion will focus on the pre-combustion, in-cylinder, and post-combustion strategies of controlling NOx emissions and particulate matter emissions.

**Figure 2.9: Emissions Control Strategies for Compression Ignition Engines [49]**
2.4.1 Pre-Combustion Strategies for Emissions Reduction

Many researchers have shown that the properties of diesel fuels in combination with engine technology can greatly affect the engine out emissions [51]. With the current research focus shifting to demonstrating alternative compression ignition fuels from non-petroleum sources in diesel engines, much research is bringing to light ways to reduce exhaust emissions, including particulate matter emissions, through changes in fuel formulation.

To enable the implementation of particulate and NOₓ control technologies, the US EPA has mandated that ultra-low-sulfur fuels be available to enable advanced aftertreatment strategies, which can be highly sulfur sensitive [52]. Modification of diesel fuel composition, for example, by blending with oxygenated fuels, also can contribute to reducing emissions. The addition of biomass-derived fuels and synthetic fuels to diesel fuel base stocks is a means of producing a cleaner burning diesel fuel. Blending with oxygenated or zero sulfur fuels can lead to particulate emissions reductions by interfering with the soot formation process and by decreasing the formation of sulfates. However, in the case of biodiesel fueling (e.g., “B20”, a blend of 20 vol.% methyl soyate in diesel fuel) there is a well documented increase of 2-4% in NOₓ emissions [53].

Hess showed that there could be 10% brake specific particulate matter reduced with just 2% oxygen addition in the fuel [54]. Hess used such oxygenates as monoglyme and diglyme, from the family of glycol ethers. Hess’s work also showed that with each 1% of oxygen blended above 2%, the improvement of the particulate matter reduction
decreases until approximately 7% oxygen blended into the fuel, and yields about 7% brake specific particulate matter reduction.

The recent requirement for fuel sulfur reduction to allow for the use of exhaust catalysts also gave way to the added benefit of particulate reduction [9, 10, 55]. Fuel sulfur has been shown to contribute to a total particulate matter mass in the form of sulfates [56].

Other alternative compression ignition fuels from non-petroleum sources are of significant interest and have been shown to reduce or increase exhaust emissions. Two of these fuels for compression ignition engines will be discussed as they are used in this research: Dimethyl Ether and Biodiesel.

2.4.1.1 Dimethyl Ether

Dimethyl ether (DME) has been considered for use as a fuel in compression ignition engines since the early 1990s. Fleisch and coworkers demonstrated a Navistar diesel engine meeting the California ULEV emissions while operating on DME [57]. The exciting results have suggested that the DME is a potential fuel for the future that can meet the stringent emissions. The following section gives a brief overview of DME.

DME is a compound that has been targeted for future use as a fuel, in several countries around the world, including Japan, China, and Sweden [58-60]. Motivation to use DME exists for several reasons. There has been confirmation that the fuel yields low particulate emissions and possibly lower NOx emissions [57, 61, 62]. In addition, DME
can be made from a variety of feedstocks including coal, biomass, and natural gas via the synthesis gas process, which can support the use of alternative energy resources [63, 64].

Compounds in which two hydrocarbon groups are bonded to one oxygen, represented as R-O-R’, are called ethers. The organic groups bounded to the ether may be alkyl, aryl, or vinylic, and the oxygen can either be in an open chain or ring configuration [65]. Ethers commonly observed in long chain structures are referred to as linear ethers. As compared to alkanes of similar carbon number, the boiling points of ethers are higher [65]. This class of oxygenated compounds have high cetane numbers and excellent cold flow properties [66].

Simply stated, dimethyl ether is an ether with a methyl group on each side of an oxygen atom. Today, it is predominantly used as an aerosol propellant because it is not harmful to the ozone layer, in contrast to the chlorofluorocarbons used previously [64]. Also, it is virtually non-toxic and is easily degraded in the upper atmosphere [67]. It can be represented by the symbol: CH$_3$O-CH$_3$. The physical properties of DME are shown in Table 2.2 along with some other fuels for comparison [57, 61, 68, 69].
The cetane number describes the ignition quality of the fuel. The shorter the ignition delay the better the ignition quality of the fuel, and thus, the higher the cetane number. Since DME has a higher cetane number than conventional diesel fuel, it will ignite readily and burn more completely.

The viscosity of DME, as a liquid, is much lower than that of diesel fuels. This offers an advantage in that the fuel will be easier to deliver into the engine cylinder than diesel fuel during cold weather conditions. However, some studies have shown that DME leaks from the fuel injectors [70, 71]. In addition, using neat DME within an engine creates some lubricating problems because of the low viscosity. Researchers are now understanding that the fuels used in automotive fuel injection systems have inherent

---

### Table 2.2: Physical Properties of DME [57, 61, 68, 69]

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
<th>Diesel</th>
<th>Propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C\textsubscript{2}H\textsubscript{6}O</td>
<td>C\textsubscript{10.8}H\textsubscript{18.7}</td>
<td>C\textsubscript{3}H\textsubscript{8}</td>
</tr>
<tr>
<td>Mole Weight</td>
<td>46.07</td>
<td>148.6</td>
<td>44.11</td>
</tr>
<tr>
<td>Critical Temperature- °C</td>
<td>127</td>
<td>-</td>
<td>95.6</td>
</tr>
<tr>
<td>Boiling Point- °C</td>
<td>-24.9</td>
<td>71-193</td>
<td>-42.1</td>
</tr>
<tr>
<td>Vapor Pressure at 20 °C-kg/m\textsuperscript{2}</td>
<td>5.1</td>
<td>&lt;0.01</td>
<td>8.4</td>
</tr>
<tr>
<td>Critical Pressure-bar</td>
<td>53.7</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>Liquid Viscosity- cP</td>
<td>.15</td>
<td>2-4</td>
<td>.10</td>
</tr>
<tr>
<td>Liquid Density at 20 °C-kg/m\textsuperscript{3}</td>
<td>668</td>
<td>800-840</td>
<td>501</td>
</tr>
<tr>
<td>Bulk Modulus (N/m\textsuperscript{3})</td>
<td>6.37E+08</td>
<td>1.49E+09</td>
<td></td>
</tr>
<tr>
<td>Specific Density, gas</td>
<td>1.59</td>
<td>-</td>
<td>1.52</td>
</tr>
<tr>
<td>Solubility in H\textsubscript{2}O at 20 °C g/l</td>
<td>70</td>
<td>Negligible</td>
<td>.12</td>
</tr>
<tr>
<td>Lower Heating Value- kJ/kg</td>
<td>28430</td>
<td>42500</td>
<td>46360</td>
</tr>
<tr>
<td>Heat of vaporization- kJ/kg 20°C</td>
<td>410</td>
<td>233</td>
<td>426</td>
</tr>
<tr>
<td>Explosion limit in air- vol%</td>
<td>3.4-17</td>
<td>1.0-6.0</td>
<td>2.1-9.4</td>
</tr>
<tr>
<td>Ignition temperature at 1 atm- °C</td>
<td>235</td>
<td>250</td>
<td>470</td>
</tr>
<tr>
<td>Cetane Number</td>
<td>55-60</td>
<td>40-55</td>
<td>-</td>
</tr>
</tbody>
</table>
lubricating traits which are a very significant factor, especially when additives and alternative fuels are being considered [72-75].

The boiling point of DME is another important advantage for its use as a fuel. Again, it proves to have better characteristics for cold starting conditions, which is a key factor in engine development.

The vapor pressure of DME is a concern. Since the fuel is a gas at atmospheric pressure, to use it as a liquid one would need to mix the fuel with a lubricity additive and inject the fuel as a liquid with the entire fuel system pressurized [76]. This leads to other complications with fuel delivery, although the technology to do this is similar in nature to LPG (Liquid Propane Gas) because LPG is also moderately pressurized to keep it in a liquid state [77].

Another important aspect of combustion emissions from a diesel engine fueled on DME versus diesel fuel, is the reduction and elimination of particulate emissions. Particulate emissions can be observed as a black smoke emitted out the tailpipe. The oxygen content of a fuel blend with DME (at roughly 40 to 100 wt.%), allows for the emissions to be smokeless, as shown in the literature [57, 61, 69, 78-81]. DME has a 34.8% oxygen content as a neat fuel. Nabi and coworkers showed “smokeless” engine operation from a diesel fuel with an oxygen content at around 38 wt. % [78]. However, work by Chen and coworkers confirms that even with 80 wt.% DME addition to diesel fuel, some smoke will be produced at high engine loads, even though it is a small amount [81].
The heating value of DME is a concern, because the heating value of diesel is roughly 1.7 times that of DME. This results in the need for more volume of fuel to produce the same output from combustion. By altering injection amounts to the cylinders, the amount can be compensated to counteract the decreased heating value and prevent “de-rating” of engine output.

Dimethyl Ether (DME) has been shown to reduce PM and NOx emissions [57, 82-86]. Not only has DME been demonstrated theoretically and experimentally to exhibit rapid reaction chemistry, but also DME has been shown to reduce NO and CO emissions in premixed flames [87]. In comparing DME with propane and butane in a fuel equivalence ratio range of 0.6 to 3.2, DME demonstrated reduced CO emissions, and less striking, NO reduction over the other two fuels. As a result of finding higher equilibrium NO concentration with DME, it was determined that this was due to a higher adiabatic flame temperature over the entire stoichiometric range in comparison to propane and n-butane[87]. However, Frye concedes that in all comparisions made on the NO emissions, DME gave at worst the same result as propane and n-butane[87].

The US does not currently have in place facilities for the manufacture of DME on a fuel production scale or the infrastructure available for the use and distribution of the fuel. This fuel has been considered in many economic models and studied as a fuel to achieve tripled fuel economy, but it is not currently a fuel being considered for use in US vehicles, and thus no on-road vehicles are in trials or production [88-92]. It has been reported that DME acts similarly as LPG fuel and the LPG fuel transport lines could be used to transport and distribute DME in a more widespread capacity [93, 94].
The research discussed in Chapter 5 uses DME as the fumigated fuel in a Mixed Mode Combustion process. That research exploits the unique low temperature ignition quality of DME.

2.4.1.2 Biodiesel

Biodiesel has received rapidly growing interest as a fuel to blend with existing diesel fuels. Biodiesel is an alternative diesel fuel created by the conversion of oils, fats and fatty acids to methyl and ethyl esters via esterification processes [95]. A variety of vegetable oils and animal fats provide the source of the triglyceride fats and oils [96]. Continuous feedstock growth and livestock production provide a constant supply of source material allowing biodiesel to be a renewable source of fuel, which can be created domestically [97].

Additionally, biodiesel is miscible with petroleum-based diesel and works in any diesel engine with little or no modifications as pure biodiesel or as a blend with any other diesel fuel. It fact, biodiesel contains a higher oxygen (~ 11 wt. %) content resulting in a more complete combustion of the fuel, reducing emissions of particulate matter, unburned hydrocarbons and carbon monoxide. Sharp and coworkers’ research showed a 40% reduction in CO emissions using neat biodiesel in modern diesel engines, while hydrocarbon emissions were eliminated [98]. They also tested a 20% biodiesel blend and found a comparable and proportional trend in the emissions [98].

While there are many benefits to biodiesel, studies have shown that engine emissions using biodiesel fuels typically increases emissions of oxides of nitrogen (NOx)
This compiled data from the US EPA is shown in Figure 2.10 [53]. For a 20% blend of biodiesel in diesel fuel, on average, a 2% increase in NOx emissions is observed. However, this EPA study was the culmination of much research on heavy duty diesel engines that have various types of diesel engine injection equipment. Research is now focused on the fuel property aspects of the biodiesel and how this affects the resultant NOx emissions. The EPA study also prompted more research into the effect of biodiesel on Light Duty Diesel engines, as this was missing from the initial review. Duffield, Shapouri, Grabowski, McCormick, and Wilson’s report, “U.S. Biodiesel Development: New Markets for Conventional and Genetically Modified Agricultural Products”, has also prompted further research into improving biodiesel in the areas of NOx emissions, viscosity, and oxidative stability to allow biodiesel to become a commercially acceptable fuel [97].

One approach to improving the properties of biodiesel fuels is to increase the degree of saturation of the ester molecules contained in the biodiesel. The saturation of the biodiesel fuel is often measured and reported as the iodine value. McCormick and coworkers showed a correlation between the iodine value and NOx emission from various biodiesel feedstocks [99]. Figure 2.11 shows the correlation developed by McCormick and coworkers between the iodine value of biodiesel from various feedstocks and the resulting NOx emissions from the use of the fuel. Researchers are pursuing modifying the soybean oil through genetic engineering of the soy plant to increase the oleic acid content [100]. Increased saturation can also be achieved by hydrogenation of the biodiesel fuel. Chapter 4 of this research presents a study of the emissions characteristics from a light duty diesel engine from the blending of a hydrogenated soy based biodiesel
with low sulfur diesel. In this research, the EGR is removed so that the NOx reduction effect of the EGR does not complicate the actual reductions or increases achieved by the fuel.

Figure 2.10: Average emissions impacts of biodiesel for heavy-duty highway engines [53]
2.4.1.3 Iodine Value of Biodiesel Fuels

The iodine number is a measure of the degree of unsaturation of the esters within biodiesel fuels [95, 99]. A fuel containing a higher degree of unsaturated esters will have more double bonds within the fatty acid chain than that of a fuel with a lower degree of saturation. According to McCormick and coworkers, a lower iodine number results in less nitrogen oxide emissions than a biodiesel fuel with a higher iodine number [99]. This correlates with his other observations because a biodiesel fuel with a higher iodine number will have a lower cetane number and a higher density [101, 102]. However, McCormick and co-workers observed that a higher degree of saturation decreased the
boiling point and viscosity of the biodiesel fuels that were tested resulting in poor cold flow properties [99].

Thus, fuel properties are very interrelated with each other and with engine performance. The fuel properties and their relationship to the combustion of the hydrogenated and normal soy based biodiesel fuel are further investigated in Chapter 4.

2.4.1.4 Theories about Biodiesel and NOx

The increase of NOx emissions as a result of the use of biodiesel in an engine has not clearly been understood. Recent reviews of the emissions results are clearly showing increases and reductions of NOx emissions depending upon engine size, fuel injection type, fuel injection strategy, and engine testing strategy. Researchers have given various explanations [103-106]. This section will explore the current explanations given for the biodiesel NOx effect. The current theories include: 1) Adiabatic Flame Temperature, 2) Flame Radiation, 3) Mixing, 4) Prompt NOx, 5) Fuel Injection Timing, 6) Cetane Number, 7) Mixture Stoichiometry at the Lift-Off Length, 8) Oxygen Content of the Fuel, 9) Fuel spray characteristics, such as droplet size and air entrainment.

**Adiabatic Flame Temperature:** The conceptual model of the diffusion or mixing controlled phase of diesel combustion suggests that NOx is formed on the lean side of the flame [29]. Dec also confirmed this model through laser based measurements [107]. Thus, the flame temperature in the diffusion zone in close proximity to the NOx formation zone has an influence on the thermal NOx formation. Some authors state that the adiabatic flame temperature of the fuel is higher for biodiesel fuels [108-110], while
others state that it is higher for diesel fuels [111, 112]. Cheng and coworkers found no significant different between methyl oleate and a primary reference fuel in calculations for the stoichiometric conditions representative of those in the diffusion flame [42].

**Flame Radiation:** The flame radiation theory relates to the reduction of soot volume fraction as a result of using a biodiesel fuel or fuel blends. Musculus showed that soot radiation from the flame zone may cool down the diffusion flame temperature and thus lead to a reduction in NOx emissions [113, 114]. Since there is less soot in the diffusion flame region during the combustion of biodiesel, this can lead to a reduction of soot radiation from the flame region and result in higher flame temperatures [113, 114]. Cheng and coworkers used spatially integrated natural luminosity (SINL) in an optically accessible single cylinder Caterpillar 3176 engine to view the change in the luminosity of the soot radiation with different fuels [42]. In their research, the timing of the start of combustion for each fuel was matched to keep the overall combustion timing the same. Their research shows that there is less luminosity for biodiesel in comparison to the reference fuel with increasing engine load, suggesting that the reduction in flame radiation may be increasing the peak flame temperature and thereby NOx emissions[42].

**Mixing:** In the literature, a connection between the premixed-burn fraction and NOx emissions has been demonstrated [113]. Musculus has shown that as the premixed-burn fraction increases, NOx emissions increase. The timing of the premixed-burn fraction can be a function of the injection timing, or more importantly the ignition delay of the fuel. A smaller premixed-burn fraction would be attributed to a shorter ignition delay.
**Prompt NO**: Prompt NO is formed by reaction of radical HC species with nitrogen, leading to the formation of NO [33]. It can account for a significant portion of the NOx formation [33]. Researchers have suggested that prompt NO (also known as Fenimore NO) is the reason for the increase in NOx emissions, and not the Zeldovich mechanism (thermal NO) [99, 115]. They speculate that during combustion of the biodiesel fuel, the double bounded molecules cause higher levels of certain hydrocarbon radicals in the fuel-rich zone of the diesel combustion spray [110]. Ban-Weiss and coworkers used numerical simulations of methyl butanoate to show that the Fenimore mechanism contributes to 13% of the overall NOx emissions [110]. They also confirmed with a comparison to methyl trans-2-butenoate that the double bond produces an increase in the flame temperature of 14 K, which resulted in a 21% increase in the NOx emissions [110].

**Fuel Injection Timing**: An advance of the start of injection due to the physical property differences between diesel fuel and biodiesel fuel has been proposed and shown to be a contributor to the NOx emissions increase [103]. Szybist and coworkers showed that this trend of injection timing advance directly correlated to a NOx increase, and explained this was due to the elevated bulk modulus of compressibility of the biodiesel fuel [116]. This work was performed with a pump-line-nozzle fuel injection system. This advance is also seen as a result of a change in the throttle position as a result of the additional biodiesel fuel required due to the reduced heating value of biodiesel [117]. While Boehman and coworkers established a relationship between the bulk modulus of the fuel and fuel injection timing [118], Szybist and coworkers concluded that the dominant effect for the particular engine being tested was the timing of maximum heat
release and maximum cylinder temperature[119, 120]. Recent work performed with a light duty diesel engine equipped with a common rail injection system showed that the system exhibited no measurable injection timing shift when biodiesel blends were used [121]. However, biodiesel blends exhibited higher maximum needle lifts, longer injection durations, and higher rail pressures to deliver the required fuel as a result of the change in heating value with biodiesel [121].

Other researchers have studied how the impact of multiple injection strategy affects NOx emissions when using biodiesel fuels. Choi and coworkers showed that at high load, a split injection strategy had no effect on NOx emissions, but at low load, NOx decreased and the effect seemed to be dependant upon the start of injection [122]. Utilization of a pilot injection is becoming important in modern diesel engines as a means to reduce the combustion noise level. The pilot injection decreases the premixed-burn fraction intensity of the combustion process. Zhang studied the pilot injection effect in a 4 cylinder DI diesel engine [123]. While his studies showed that the NOx emissions could be reduced with the use of EGR and without pilot, there was an increasing amount of smoke emissions with the pilot injection and a slight increase in the NOx emissions [123]. Zhang looked at the change in the interval between the pilot and the main injection and saw little change in the NOx emission level, showing that this can be used to reduce combustion noise and have no effect on NOx emissions [123]. Senatore and coworkers showed in their work that “by varying injection start advance and EGR percentage” for biodiesel, these were effective measures to produce the same NOx emissions produced from a EURO IV Common Rail Diesel Engine [124].
**Cetane Number**: Biodiesel fuel tends to have a higher cetane number than diesel fuels. Based on this data, it would be expected that biodiesel would reduce the NOx emissions since it would produce a shorter ignition delay and thus a shorter premixed-burn fraction [42]. Hence, cetane number alone may not be an effective measure of the ignition behavior of the fuel.

**Mixture Stoichiometry at the Lift-Off Length**: Cheng and coworkers suggest that the mixture stoichiometry at the lift-off length of the fuel from the injector nozzle may be different between diesel and biodiesel and thus plays a role in the NOx increase, but the mechanisms for this are unknown [42]. Choi and Reitz showed though numerical simulation that the spray tip penetration and fuel mass injections increase with biodiesel blended in diesel fuel [125].

**Oxygen Content of the Fuel**: Some researchers suggest that the higher oxygen availability in the combustion chamber as a result of the oxygen in the fuel contributes to the NO formation process [126, 127]. Schmidt and coworkers showed that enriching the intake air with oxygen led to the same NOx increase exhibited with the increase in oxygen of the biodiesel fuel. Iida and coworkers also showed an increase in NOx emissions with an increase in the oxygen in the intake air. Song and coworkers showed that both the enrichment of the intake air and the oxygenated fuel gave an increase in the NOx emissions [128]. The increase was higher for the enriched intake air than for the use of the oxygenated fuel. Other researchers argue against the presence of oxygen in the fuel as an explanation of the NOx increase. Lupuerta and coworkers made this conclusion because the diffusion combustion is occurring in regions of stoichiometric oxygen-fuel ratio, and thus the oxygen in the fuel is not enough to make a difference in
the flame chemistry[108, 129]. Yuan and coworkers tried to find a correlation between NOx and fuel oxygen content, but were unsuccessful [130].

**Fuel Spray Characteristics:** The fuel spray characteristics, including droplet size distribution, droplet inertia, air entrainment, penetration in cylinder, evaporation rate, and heat dissipation are affected by the various fuel properties [95]. These fuel properties include viscosity, surface tension, cetane number, and the boiling range temperature of the fuels [95]. These physical phenomena have some influence on the ignition delay time, and thus on the premixed-burn fraction/diffusion combustion ratio and in turn on the NO formation process [103]. If cetane number is not an effective measure of the ignition behavior of the fuel, then there are other fuel properties that would affect the premixed-burn fraction of the fuel and increase the NOx emissions, in spite of the higher cetane number of the biodiesel fuel [42]. As mentioned previously, Choi and Reitz showed through numerical simulation that blends of biodiesel fuel require higher fuel mass injection rates and thus produce increased spray tip penetration in the cylinder [125]. This effect of mixing of a biodiesel fuel type and spray penetration into the cylinder was also shown by Yuan and coworkers [130].

### 2.4.2 In-Cylinder Combustion

There are several techniques which can aid in reducing NOx emissions in the cylinder during the combustion process. These include exhaust gas recirculation (EGR), injection timing control, and fuel injection rate shaping [131-133]. The goal of these three techniques is to reduce the peak flame temperature which leads to thermal NOx or
to reduce the time for the thermal NO reaction while still achieving the best BSFC for the particular engine condition. However, these techniques also have drawbacks. In altering the fuel injection timing to the cylinder, power decreases and fuel consumption increases. Also, reducing the peak flame temperature causes an increase in the level of soot emissions, due to the reduced kinetic rate for soot oxidation [49].

There are several new techniques being explored to simultaneously reduce the soot and NOx emissions from the combustion process. These include Low Temperature Combustion (LTC), Homogeneous Charge Compression Ignition (HCCI), Premixed Controlled Compression Ignition (PCCI). Both LTC and PCCI have been shown to give high NOx reduction and low particulate emissions [134]. PCCI differs from HCCI in that a direct injection of fuel prior to the main injection achieves air/fuel mixture gradients that are not truly homogeneous as in HCCI [135]. High levels of EGR are also associated with LTC and PCCI modes. Hardy and Reitz combined the effects of PCCI and diffusion-controlled diesel combustion to achieve emissions levels below the 2010 emission standards [135]. A map of the local combustion temperature and local equivalence ratio shows the range characteristics of the different combustion modes [134]. This map is shown in Figure 2.12.
2.4.2.1 Homogeneous Charge Compression Ignition (HCCI)

Homogeneous Charge Compression Ignition (HCCI) combustion occurs when a mixture of air and fuel, and sometimes recycled combustion products, is compressed until it autoignites [136]. The result is heat releasing reactions that initiate simultaneously at multiple sites in the combustion chamber. In contrast to diesel (diffusion–controlled) combustion, HCCI reactions are not limited by the mixing rate at the interface between the jet of fuel and the surrounding oxidizer. HCCI combustion differs from spark-ignited combustion because it has no discernible flame front and it has no localized high temperature reaction region [137].

For the purpose of the research involved in this project, the following definitions are introduced. Induction of a fuel and air mixture into an engine cylinder during the
intake stroke, and the compression of that mixture to ignition is referred to as homogenous charge compression ignition or HCCI. When using a diesel pilot as the ignition source for the homogeneous charge, the combination of combustion strategies is referred to as mixed mode combustion.

2.4.2.2 Variables involved in HCCI process

HCCI combustion displays a particular heat release curve with two distinct stages. The first stage of the heat release is associated with low temperature kinetic reactions (cool and/or blue flame) [136]. The time delay between the first and the main heat release is attributed to the negative temperature coefficient regime of the reactions [138, 139]. An example of the combustion parameter diagram is shown below in Figure 2.13 [140]. Research has shown that HCCI combustion initiates simultaneously in multiple locations in the cylinder and that there is no discernable flame propagation [138]. Most researchers believe that HCCI heat release is purely controlled by chemical reactions [136]. Since the reactions are not initiated by spark ignition and not limited by traditional flame sheet physics, leaner mixtures can be used in HCCI combustion [136].
Management of HCCI combustion in a practical system is a function of controlling the autoignition of the fuel which is dictated by the location of the low temperature reactions which then function to generate the high temperature reactions in the main heat release. Therefore, it is important to control the low temperature reactions [141]. Researchers have offered several methods to accomplish this, which include controlling the intake air temperature, modify the fuel blending, or turbocharging/supercharging the intake air charge [142, 143]. These are specific methods to modify the initial temperature of the fuel and air charge, without significant modifications to the engine, as would be required to implement variable compression ratio or variable valve timing [136, 144].

Figure 2.13: Definition of the combustion parameters [140]
2.4.2.3 Types of Fuel Mixture Preparation for Compression Ignition Combustion

Throughout the development of the HCCI concept, there have been limitations discovered with the process. These include the increase in hydrocarbon and carbon monoxide emissions, the limitation on engine load that can be achieved both on the low end of operation (speed and load that operate the engine below 2.0 bar IMEP) and the high end of operation (speed and load the operate the engine above 3.5 bar IMEP) [145], and the ability to control ignition of various fuel types. Therefore, researchers have tried to resolve the issues with different types of fuel mixture preparation for compression ignition combustion which include HCCI–like concepts and testing with various fuels:

- Fuels (liquid and gaseous): Gasoline, diesel, naphtha, natural gas, butane, propane
- Fuel introduction: micro-atomization in air induction, fumigation, direct injection in cylinder
- Mixing: Homogeneous, partial mixed [135, 146]
- Ignition initiation: Through the compression of the fuel, initiated by a spark, initiated by a pilot injection

Though there have been many researchers working on the same issues over the last 10-15 years, some of the same questions still remain. Most importantly, the kind of fuel appropriate for the HCCI process and how to control the ignition behavior of the fuel [145, 147, 148]. Additionally, the benefits for emissions reductions have not always been successfully demonstrated across all engine platforms, lending further support for continued research.
2.4.2.4 HCCI engine and Dual Mode Processes

A suggested method to increase the operating range of an engine operating with the HCCI process is to prepare it to run in a dual mode process. This can mean two things: 1) that the engine operates with two different combustion processes over the entire range of operation of the engine, and 2) that the engine operates in HCCI with a pilot injection, as a dual fuel engine, with the injection occurring inside the intake air system just prior to entry into the cylinder or directly into the cylinder. Stanglmaier and coworkers at Southwest Research Institute developed a dual fuel natural gas engine to operate in HCCI mode at idle to mid range operation to improve fuel efficiency and reduce NOx emissions [149]. Although the goal of the experimentation was achieved, higher levels of HC and CO emissions were also observed [149]. Park and coworkers at West Virginia University developed a dual fuel engine based on the Navistar T444E [150]. The engine was fumigated with natural gas, and the diesel injection system was operated to bring in diesel fuel at a different timing scheme than the original engine [150]. Although they were successful in reducing NOx and particulate matter emissions, the HC and CO emissions increased substantially over the diesel-only levels [150].

2.4.2.5 Mixed Mode Combustion

There is also another style of combustion that is being explored. In the literature, some researchers call it the dual fuel engine, whether those fuels are gaseous or liquid or a combination of both [151-154]. In each of these researchers’ work, diesel or biodiesel fuel was used as a “pilot” fuel, a gaseous fuel is inducted or injected into the cylinder,
and a pre-mixed gaseous fuel and air mixture is compressed. While this may sound similar in nature to conventional pilot and main fuel injection in a diesel engine, the benefits of a dual fuel engine are only now being researched and understood. Karim has postulated a schematic representation of the energy release rate for this type of combustion strategy [151]. In his schematics for both a light load and a heavy load condition, he shows three phases of the energy release: 1) phase one is due to the combustion of the pilot fuel, 2) phase 2 is due to the combustion of the gaseous fuel that is in the immediate vicinity of the pilot combustion, and 3) phase 3 is due to any preignition reactions and the turbulent flame propagation within the lean mixture [151]. Karim’s research focused on using primarily propane, hydrogen, and methane as the gaseous fuel, with the primary focus on methane, and emissions characteristics and combustion analysis [151].

Chapter 5 of this thesis focuses on a similar kind of dual fuel engine, referred to here as a mixed mode combustion process. In this research, DME is the fuel being inducted into the engine and diesel is the pilot fuel. In this process, a low temperature combustion mode is initially achieved with a secondary diffusion mode of diesel combustion. However, the low temperature combustion was not achieved with the aid of high levels of EGR or cooled EGR. It is hypothesized that, through the use of the ignition properties of the fuel and early low temperature heating in the cylinder, a reduction in NOx emissions can be achieved.
2.4.2.6 Ignition Delay

An important property of the fuel is its ignition delay, or the time from which the fuel begins to be injected into the cylinder until some detectable heat release occurs. Time is required to sufficiently mix the fuel and air present in the cylinder, and then chain initiation reactions take place so that the chemical explosion begins to occur and the chain propagation reactions begin to increase in number [11]. Researchers have tried to understand the factors that affect the ignition delay so that this could be used to better control the combustion process regardless of fuel type [11]. The standard equation used to describe ignition delay is shown in Eq. 2.20. In this equation, \( \tau_{id} \) is the ignition delay, \( E_A \) is the apparent activation energy for the fuel autoignition process, \( \bar{R} \) is the universal gas constant, \( p \) is pressure, and \( A \) and \( n \) are constants dependent on the fuel, fuel injection, and air flow characteristics [11]. Heywood goes on to explain that there are many factors that affect the ignition delay, including mixture temperature, pressure, and equivalence ratio. This is the typical equation used for data from combustion bombs and flow reactors [11].

\[
\tau_{id} = Ap^{-n} \exp\left(\frac{E_A}{\bar{R}T}\right)
\]  

Other correlations for predicting ignition delays have been prepared based on empirical formulas and give good agreement over a wide range of engine conditions. One developed by Hardenburg and Hase predicts the ignition delay based on the cetane number of the fuel and the temperature and pressure during the delay at top dead center (TDC) conditions [155]. This equation from Hardenburg and Hase along with a
refinement from Prakash and coworkers [156] provided Garnier and coworkers an
equation that was able to model the ignition delay for a syngas dual fueled engine above a
30% substitution of the fuel [157]. The authors claim good agreement at 30% and above,
but their figures show a margin of 1 crank angle degree above 50% substitution of the
fuel between the experimental and predicted ignition delay, which indicated good
agreement within a margin of 1 crank angle degree [157].

Karim has shown in his research the effect of the fuel and air mixture on the start
of combustion timing in a dual fuel engine mode for various fuels [151]. While methane
and hydrogen exhibited little change in the start of combustion timing over the various
stoichiometric ratios, the start of combustion timing for ethylene and propane over
various stoichiometric ratios varied widely [151].

2.4.3 Post Combustion

2.4.3.1 NOx Aftertreatment Devices

The general method which exists for controlling NOx via post-combustion
techniques involves some type of catalytic reaction, chemical reaction or a combination
of both. There are two types of catalytic reduction: Selective Catalytic Reduction (SCR),
and Selective Non-Catalytic Reduction (SNCR), both thermal and non-thermal [50]. The
method that is most widely being considered is the SCR method, also most commonly
known as DeNOx Catalysis. In this method, a zeolite catalyst is used to absorb NOx
molecules. A reagent is injected into the exhaust stream to chemically reduce the NOx.
Previously, the typical reagent used was the fuel itself, which reduces the efficiency of
the vehicle. However, it is common now to use urea. It should be noted that this process
works in a small temperature band (200-250 °C for precious metal zeolites and 400-450
°C for base metal zeolites), and for vehicles the NOx reduction is low and selectivity is
poor [158].

The predominant method of selective catalytic reduction uses ammonia or urea as
the reductant [159]. Studies with these types of catalyst applications have shown 90%
reduction and higher can be achieved with an SCR catalyst and urea as the reductant
[160, 161]. Testing has been completed using SCR, EGR, and intensive engine mapping
which resulted in dramatic reduction of NOx emissions [162].

The following reactions, Eq. 2.21 through Eq. 2.25, describe the primary chemical
reactions that occur in the ammonia SCR system. All of these reactions are occurring in
the catalyst to reduce NOx down to elemental nitrogen and water. Reaction Eq. 2.22 is
the dominant mechanism for NO reduction [163].

\[
\begin{align*}
6\text{NO} + 4\text{NH}_3 &= 5\text{N}_2 + 6\text{H}_2\text{O} \tag{2.21} \\
4\text{NO} + 4\text{NH}_3 + \text{O}_2 &= 4\text{N}_2 + 6\text{H}_2\text{O} \tag{2.22} \\
6\text{NO}_2 + 8\text{NH}_3 &= 7\text{N}_2 + 12\text{H}_2\text{O} \tag{2.23} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 &= 3\text{N}_2 + 6\text{H}_2\text{O} \tag{2.24}
\end{align*}
\]
Current research is focusing on the use of SCR with urea as the reductant and Lean NOx traps (LNTs) to meet emissions in Europe for 2009 and beyond, with technology which can also be applied to vehicles in the US market [164]. For vehicle aftertreatment, a combination of LNTs and SCRs is also being considered, with the LNT being used to provide ammonia to the SCR during rich regenerations [164]. For heavy duty engines, exhaust temperatures are high enough to provide the heat necessary for the urea to hydrolyze to ammonia and for reactions to take place. However, in light duty diesel engine applications, exhaust temperatures are too low for appropriate operation of the NOx reduction with either a LNT or SCR in conjunction with particulate matter reduction over the catalyst [165, 166]. To achieve ULEV II standards (.05 g/mi NOx), Tennison and coworkers used a fast warm up routine with the engine to gain the required light off temperature for the SCR within the first 100 seconds of operation [167]. Ogunwumi and coworkers are working on in-situ methods via an ammonia generating catalyst to generate ammonia so that urea is not required as an added on board reductant [168].

2.4.3.2 Particulate Matter Aftertreatment Devices

Diesel particulate emissions pose a significant potential health hazard. Control of diesel particulate emissions is an issue requiring the attention of the fuels, engine and aftertreatment industries. To achieve the reductions in particulate emissions mandated by

\[
\text{NO + NO}_2 + 2\text{NH}_3 = 2\text{N}_2 + 3\text{H}_2\text{O}
\]
the US Environmental Protection Agency in 2007, use of diesel particulate filters (DPF) will be a necessity [169].

There are two groups of diesel exhaust aftertreatment devices: particulate traps and diesel oxidation catalysts. Diesel particulate traps, which are primarily filters, control diesel particulate matter emissions by physically trapping the particulates. The major challenge in the design of a diesel particulate trap system is to regenerate the trap by oxidizing the collected particulate matter in a reliable and cost-effective manner [170]. A critical requirement for implementation of diesel particulate filters on diesel-powered vehicles is having a low “break even temperature”, or balance point temperature, defined as the temperature at which particulate deposition on the filter is balanced by particulate oxidation on the filter and indicated by exhaust restriction. This balance point needs to occur at sufficiently low temperatures to fit within the exhaust temperature range of a typical diesel vehicle’s duty cycle. Catalytic coating on the diesel particulate filter, use of a fuel-borne catalyst and oxidation catalysts placed upstream of the particulate filter can all reduce this balance point temperature [171].
Chapter 3
Experimental Setup

3.1 Introduction

This chapter provides details of the experimental set up and the methods used for this research. First, the general engine system used for both experiments will be described. Further detail on modification to the engine systems for each experiment are contained in the respective chapters. Then, a detailed description of the equipment used for the collection of the experimental data will be provided in additional sections. A review of the engine and emissions equipment repeatability will be discussed.

3.2 Engine Description

A Detroit Diesel Corporation (DDC) 2.5 L 4-cylinder turbocharged direct injection engine (built by VM Motori, Italy) was used for both experiments described in the Chapters 4 and 5. The engine, made for the European market by VM Motori, was purchased by DDC and was sold to Chrysler for inclusion in their Jeep Cherokee CJ vehicles for the European and South American markets. The engine is configured with a Bosch common rail fuel injection system. It is shown below coupled with the 5 speed manual transmission in Figure 3.1. The performance curve of the engine is shown in Figure 3.2.
Figure 3.1: Detroit Diesel Corporation 2.5L Engine

Figure 3.2: Engine Rating of the 2.5L Detroit Diesel/ VM Motori Engine [172]
The DDC 2.5L engine is described in Table 3.1. The standard fuel injection strategy is comprised of a pre-injection followed by a main injection to reduce emissions and engine noise.

<table>
<thead>
<tr>
<th>Engine</th>
<th>DDC 2.5L TD DI-4V automotive diesel engine</th>
</tr>
</thead>
<tbody>
<tr>
<td>Displacement</td>
<td>2.5L</td>
</tr>
<tr>
<td>Bore</td>
<td>92mm</td>
</tr>
<tr>
<td>Stroke</td>
<td>94mm</td>
</tr>
<tr>
<td>Compression Ratio</td>
<td>17.5</td>
</tr>
<tr>
<td>Connecting rod length</td>
<td>159mm</td>
</tr>
<tr>
<td>Rated Power</td>
<td>103KW at 4000 RPM</td>
</tr>
<tr>
<td>Peak Torque</td>
<td>340Nm at 1800 RPM</td>
</tr>
<tr>
<td>Injection system</td>
<td>Electronically controlled common-rail (Bosch)</td>
</tr>
<tr>
<td>Valve train</td>
<td>4 valves/cylinder</td>
</tr>
<tr>
<td>Intake Valve Opens</td>
<td>15.6° ATDC</td>
</tr>
<tr>
<td>Intake Valve Closes</td>
<td>64.4° ABDC</td>
</tr>
<tr>
<td>Exhaust Valve Opens</td>
<td>66° BBDC</td>
</tr>
<tr>
<td>Exhaust Valve Closes</td>
<td>32° ATDC</td>
</tr>
</tbody>
</table>

A 250HP Eaton eddy current water-cooled dynamometer was coupled to the 2.5L DDC engine to generate load. The engine and dynamometer were controlled by a Digalog Testmate control unit.

### 3.3 Engine Test Stand Data Acquisition

A time based data acquisition program was managed using a custom programmed National Instruments Labview virtual instrument (VI). The data acquisition program was set up to collect the steady state operational data from the engine’s operation. The VI was created to capture the engine and exhaust status via analog signals from pressure...
transducers, thermocouples, and serial communication from the fuel scale and emissions equipment. The signal inputs were located on a series of external computer modules, which were a collection of National Instrument Field Point Modules connected to a command module (FP-2015) to run the VI, and save the data. The data collected by the Field Point Modules was saved every 10 seconds during 20 minutes of sampling per test. Information regarding fuel consumption by the engine was collected by this program via serial communication. Gaseous emissions measurements from the ALV CEB II were collected via serial communication and also recorded.

3.4 Diesel Fuel Flow Rate

The engine fuel consumption was measured using a Sartorius model EA60EDE-IOUR precision scale that has an accuracy of ± 2g. The custom LabView VI calculated the diesel or biodiesel fuel consumption rates based on 100 measurements of fuel tank mass, tracking the small change in mass over 60 seconds.

3.5 Engine Control Unit

The electronic control unit (ECU) is the computer that controls engine operation. An unlocked ECU was used to modify and control main injection and pilot injection timings, as well as, EGR valve position, and fuel rail pressure. The unlocked ECU was connected to an ETAS MAC 2 unit via an ETK connection. The MAC 2 unit was
connected to a PC running ETAS INCA v5.0 software. INCA managed the ECU modifications in real-time.

3.6 Exhaust Gas Recirculation

The DDC 2.5L engine regulates exhaust gas recirculation (EGR) rates using an ECU map based on engine speed and injection volume. The ECU map dictates the flow rate by varying the amplitude of the signal sent to a proportional pneumatic valve. The stock DDC 2.5L engine then introduces EGR to the intake manifold via a Y-pipe. When EGR was used in the experiment, the ECU was allowed to control the EGR per the ECU map. When the EGR was not used, the EGR signal to the proportional pneumatic valve was disconnected.

3.7 Gaseous Emissions Equipment Description

3.7.1 Gaseous Emissions: AVL Combustion Emissions Bench II (CEB II)

Gaseous emissions were measured using analyzers integrated into an AVL Combustion Emissions Bench II (CEB II) emissions bench. Exhaust gases were kept at a constant temperature of 190°C with a heated sample line. NOx emissions were measured without exhaust cooling using an EcoPhysics chemiluminescence analyzer. A portion of the sample gas was chilled to remove moisture from the sample before being analyzed with Rosemount CO (IR), CO2 (IR), and O2 (paramagnetic) detectors. NO2
emissions were determined by subtracting the NO result from the total NOx result. Total hydrocarbons and methane were also collected on separate ABB Flame Ionization Detectors (FID) analyzers. All gaseous emissions were sampled continuously throughout the testing and measurements were automatically logged by the data acquisition system every 10 seconds via serial communication.

Each analyzer has a separate calibration range. Those are shown in Table 3.2. Each analyzer has a 1% of full scale instrument error, in addition to an R2 % error in the calibration curve of the instrument.

<table>
<thead>
<tr>
<th>Species</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>THC (Total Hydrocarbons)</td>
<td>930 ppm</td>
</tr>
<tr>
<td>O₂</td>
<td>24 %</td>
</tr>
<tr>
<td>CH₄</td>
<td>9920 ppm</td>
</tr>
<tr>
<td>CO₂</td>
<td>19.10 %</td>
</tr>
<tr>
<td>CO- Low</td>
<td>2451 ppm</td>
</tr>
<tr>
<td>NOₓ</td>
<td>4557</td>
</tr>
<tr>
<td>NO</td>
<td>4557</td>
</tr>
</tbody>
</table>

3.7.2 Gas Chromatography (GC)

Gas chromatography is a type of chromatography in which the mobile phase is the carrier gas, such as helium, and the stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a glass or metal tubing, called a column [173]. The chemical constituents of the sample gas pass in the carrier gas stream at different rates depending on their various chemical and physical properties and their interaction with the specific column filling. As the chemicals exit the end of the column, they are detected
and identified electronically by the calibrations that have been made in the software based on retention time, and detector response. The stationary phase in the column functions to separate different components that pass through the column and exit at a different time, which marks the retention time of the species [174].

Gaseous emissions were collected in a HP 6890 Series GC that was configured with 2 Haysep D packed columns (stainless steel, 100/125 mesh size, 1/8" diameter) with different lengths (10 and 36 ft) for both the flame ionization detector (FID) and the thermal conductivity detector (TCD). The shorter column was used in conjunction with the FID for analysis of hydrocarbons, while the longer column was used with the TCD for analysis of permanent gases and water.

The GC method used for this testing involved cooling the system to -15°C with liquid nitrogen, and then collecting data for 17 minutes at this temperature. Next, the GC went through a ramp stage from -15°C to 225°C at 30°C per minute for a period of 7 minutes. Then, at the 25 minute mark, the system was at 225°C, and continued at this temperature for 10 minutes. At the 35 minute mark, the testing was complete. The inert carrier gas used was argon (30 ml/min for the first 16 minutes, and 60 ml/min for the remainder of the test). The GC method used was configured for previous research and worked for this particular testing. Although it was not the goal of this research to improve the existing method, the method provided information about this research, specifically the amount of DME left in the exhaust emissions.

The GC chromatograms from the FID can give an indication of the change in the type of light hydrocarbons in the exhaust emissions for the C1-C6 range or species with a molecular weight less than or equal to a C6 compound [175]. In contrast, the AVL CEB
II gives bulk hydrocarbon concentrations for all hydrocarbons that are in the gaseous exhaust stream and that do condense below 190° C.

3.7.3 Fourier Transform Infrared (FTIR) Spectroscopy

Exhaust gas analyses was completed using a Nicolet Magna 550 Fourier Transform Infrared (FTIR) Spectrometer. The FTIR spectrometer was calibrated to analyze for a range of 0-200 ppm of N₂O. The spectrometer cell temperature was maintained at approximately 132 ± 5 °C to prevent water from condensing from the exhaust gas. The spectrometer cell pressure was maintained at approximately 680 ± 5 mm Hg with a vacuum system and bypass balance valve.

Throughout testing, the spectrum background was updated approximately every 60 minutes. Spectrum background sampling provided a reference point in terms of both the ambient and spectrometer operating conditions. Spectrum background updates consisted of purging the FTIR cell with N₂ for two minutes and then collecting a background spectrum.

For each RPM/engine load data point, three spectrum traces were recorded. The gaseous emissions concentrations obtained from each of the three sample traces were then averaged to obtain a representative concentration value for the particular RPM/engine load value.
3.8 Particulate Matter Emissions Equipment Description

3.8.1 Particulate Emissions: Gravimetric Filters

Particulate matter data was collected using a Sierra Instruments BG-2 Micro-Dilution Test Stand, shown in Figure 3.3 [176]. A probe collects a sample of exhaust to be analyzed. From the probe, the exhaust travels to a dilution tunnel that contains channels through which shop air is forced to quench the exhaust and dilute the particulate matter. The quenched sample is then deposited onto a filter. Finally, the exhaust gas is routed into the stand to determine other parameters such as temperature and mass flow [176].

Figure 3.3: Sierra Instruments BG-2 Micro-Dilution Test Stand [176]
The type of filter used is a Pallflex 90 mm membrane filter. Each one is weighed and placed in a humidity chamber with a constant temperature, set at 25°C and 45% RH, for at least 24 hours before it is used. After a sample is collected, the filter is placed back into the chamber for another 24 hours and weighed again. From these measurements, the mass emissions of the particulate matter can be determined.

The BG-2 test stand must be set up before each day of testing. This includes a 20-minute computer warm up period and a 60-minute continuous purge of the sample line to clear out any debris from a previous day’s sampling. A normalization filter is then used before taking actual data to clear out any residual debris from the line [176].

Setting up the dilution ratio is crucial to how much particulate matter is deposited onto the filter. Too low a ratio and not enough particulate matter will be deposited to reach an accurately measurable quantity, and vice versa. This ratio ensures at least 100 milligrams will be accumulated on the filter.

The engine must reach steady-state conditions (exhaust temperature stabilization) before taking a data point to ensure a fair reading. The exhaust is sampled for seven minutes, after which the BG-2 line valves are closed to protect the filter from any sudden pressure increase that could damage the filter and ruin the data point [76].

For the testing described in this thesis, particulate matter (PM) emissions were measured by sampling the exhaust using a Sierra Instruments BG-2 mini-dilution tunnel with a constant dilution air/sample flow ratio of 6:1, and a total flow of 60 L/min for a period of 7 minutes. Filters were collected from the sampling for gravimetric analysis and visual inspection. For each condition, only two filters were collected, weighed and analyzed accordingly. While this provides an indication of the change in particulate
mass, it is not meant to give statistically significant results which would require 6 or more filters per test.

### 3.8.2 Particulate Emissions: Tapered Element Oscillating Microbalance (TEOM)

Particulate matter (PM) emissions were measured by sampling the exhaust using a Sierra Instruments BG-2 mini-dilution tunnel with a constant dilution air/sample flow ratio of 6:1, and a total flow of 60 L/min. A portion of the diluted exhaust gas (3 L/min) was passed to a Rupprecht & Patashnick Tapered Element Oscillating Microbalance (TEOM) Series 1105 PM analyzer which measures the real-time particulate mass concentration (mg/m³). PM is collected on a Teflon filter # TX40/57-007224-0020 sold by Thermo (formerly Rupprecht & Patashnick). The software collects data on mass every half second as mass concentration (mg/m³) and translates that data into mass rate (g/sec) and total mass (g). The analyzer includes an inertial balance that directly measures the mass that is collected on a filter cartridge. The instrument monitors the change in the natural oscillating frequency of a tapered element over time as mass is collected on the filter. The instrument is set to 3 L/min flow for exhaust gas, with the mass transducer temperature, internal head, and heated sample tube temperatures set at 50°C. Data is collected every 0.1 sec for mass rate and mass concentration averaging, with total mass being averaged at every 10 seconds. The instrument can be used for transient and steady state PM emissions PM measurements. Configuration files of the equipment and software are found in Appendix A.
3.8.3 Particulate Matter Emissions: Scanning Mobility Particle Sizer (SMPS)

The TSI 3936 scanning mobility particle sizer (SMPS) spectrometer measures particle size and number density from .0025 to 1.0 μm, and from 1 to \(10^8\) particles/cm\(^3\), respectively. The data is collected and displayed in up to 167 actual channels, or 64 channels per decade. The SMPS system includes the TSI series 3080 Electrostatic Classifier with a Differential Mobility Analyzer (DMA) and a series 3776 Condensation Particle Counter (CPC). Aerosol Instrument Manager software is provided to simplify set up of the system, operation, data collection and analysis. The SMPS has also been coupled with a Dekati series 3065 Thermal Denuder.

Before the sample enters the SMPS, it passes through the thermal denuder. Depending on the temperature setting of the instrument, hydrocarbons that have agglomerated on the particulate matter are volatilized off of the particles as the sample passes through the packed carbon bed. When entering the SMPS system, the sample initially passes through a single stage impactor to remove large particles outside the measurement range. Next, the sample passes through a bipolar ion neutralizer to create a high level of positive and negative ions. The charged and neutral particles then enter the DMA in which the particles are separated according to their electrical mobility. Neutral particles exit the DMA with the excess air. Particles with negative charges are repelled towards and deposit on the outer wall of the DMA. Particles with positive charges are attracted towards the inner electrode. Particles within a narrow range of electrical mobility have the ability to pass through a narrow slit opening near the bottom of the DMA. After the aerosol particles exit the DMA, they enter the CPC and are counted.
Through the ramping of the voltage of the inner electrode exponentially over a selected period of time defined by the test, the entire particle size distribution and number concentration are measured.

The particular instrument configuration used to collect the data in this experiment is shown in Table 3.3. The SMPS was connected to the exhaust system of the DDC engine in combination with the Sierra Instruments BG-2. The BG-2 provided the vacuum to deliver the appropriate sample to the SMPS, and was adjusted to provide a 6:1 dilution ratio across the dilution tunnel filter system. Four samples were collected for each data point. The first two samples were discarded, and the remaining two points were averaged for the data presented in the figures.

Table 3.3: SMPS Property configuration for data collection

<table>
<thead>
<tr>
<th>Hardware Setting</th>
<th>Value</th>
<th>Units</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impactor Type</td>
<td>0.071 cm</td>
<td></td>
<td>For Flow rate between 1.0-2.2 lpm</td>
</tr>
<tr>
<td>Sheath Flow</td>
<td>14 lpm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol Flow</td>
<td>1.4 lpm</td>
<td></td>
<td>Set below maximum of 1.5 lpm; BG-2 set to compensate for this flow at a dilution ratio of 6:1</td>
</tr>
<tr>
<td>Size Range</td>
<td>6.26 - 237.1 nm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Voltage Range</td>
<td>11 - 9848 V</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan Up time</td>
<td>90 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scan Retrace time</td>
<td>30 sec</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scheduling</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Scans per Sample</td>
<td>1</td>
<td></td>
<td>Manual Triggering</td>
</tr>
<tr>
<td>Number of Samples</td>
<td>4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total Sample Time</td>
<td>8 min</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Physical Properties</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Particle Density</td>
<td>1.2 g/cc</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas Viscosity</td>
<td>1.32 e-05 kg/(m s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mean Free Path</td>
<td>6.65 e-08 m</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
3.9 Fuel Injection Needle Lift and Cylinder Pressure Data Collection and Analysis: AVL IndiCom

Pressure traces were collected from each cylinder at .1 crank angle resolution with an AVL GU12P pressure transducer connected to a Kistler 5010 Dual Mode charge amplifier. The pressure transducers were located in the glow plug hole for each cylinder. The amplifier signal was collected by an AVL 621 IndiModul, which is a high speed data acquisition system that records the data in real time. An AVL 365C Crank Angle Encoder is connected to the engine crank as a means to synchronize the pressure trace to the crank angle degree and top dead center. The final data form the Indimodul is sent to a PC connected to the system. The real-time data file can then be saved by the AVL IndiCom 1.3 software with Concerto 3.90 as a set of pressure traces and as an averaged file.

For this research, a set of 200 pressure traces was collected and then saved. The set of 200 traces were then averaged into one single trace and then saved. With the IndiCom software, the pressure traces can be analyzed for many pieces of information of interest from the combustion process, including heat release.

IndiCom uses the first law of thermodynamics for calculating the rate of heat release from the volume and pressure data collected by the Indimodule. Losses are neglected. The ratio of specific heats, gamma, used in the equation for the heat release in the IndiCom equation is 1.37 for a diesel engine. The apparent rate of heat release algorithm is given in Eq. 3.1, with further explanation referenced from the AVL IndiCom manual and found in [177].
\[ Q_i = \frac{K}{\kappa - 1} \left[ \kappa \cdot P_i \cdot (V_{i+n} - V_{i-n}) + V_i \cdot (P_{i+n} - P_{i-n}) \right] \]

Where:

- \( n \) is the interval (0.1 degree)
- \( \kappa \) is the polytropic coefficient \((\kappa = \frac{c_p}{c_v})\) where \( c_p \) is the temperature at a constant pressure and \( c_v \) is the temperature at a constant volume of the fuel
- \( P \) is the cylinder pressure
- \( V \) is the volume

As Heywood explains, a typical range of values for gamma for diesel heat release analysis is 1.3 to 1.35 [11]. However, the gamma will change values based on the constituents that are in the cylinder at a particular time during the compression and expansion strokes [11]. Heywood goes on to say that the appropriate value for gamma that will give the most accurate heat release is not well defined [11].

A Hall-effect needle lift sensor provided by Wolff Controls Inc. was used to obtain the injector needle lift of Cylinder 1. This signal was brought into the AVL 621 Indimodul, which was triggered by a crank angle signal from the AVL 365C angle encoder placed on the crankshaft. The real-time Indimodul data was transferred to the PC with the AVL IndiCom 1.3 software and Concerto 3.90 for further analysis.
3.10 Description of Experimental Tests

The detailed descriptions of each experiment and engine test conditions are given within the chapter for each experiment. However, a brief description of the testing will be reviewed. Each experiment had a different set of engine testing conditions, in addition to some changes to the base engine configuration, or change in fuel injection strategy for the testing. Fuel property information is found in Appendix C.

For the research performed in Chapter 4 with the hydrogenated biodiesel, the first set of experiments was performed without Exhaust Gas Recirculation over 4 operating modes with the following test conditions shown in Figure 3.4:

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Speed (rpm)</th>
<th>Load (ft-lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>1660</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>1660</td>
<td>125</td>
</tr>
</tbody>
</table>

Figure 3.4: DDC 2.5 L Engine Test Specification for NOx Reduction with Fuel Modification Experiments: Hydrogenated Biodiesel

The second set of tests with the hydrogenated biodiesel were performed at one engine mode: 1800 rpm and 61 ft-lbs of torque with a single pulse injection at 7° BTDC and without Exhaust Gas Recirculation.

For the research performed in Chapter 5 with the mixed mode combustion process, the tests were performed at one engine mode: 1800 rpm and 61 ft-lbs of torque with a single pulse injection at various timings BTDC and without Exhaust Gas Recirculation.
3.11 Repeatability Study of Engine

The engine was operated over a period of days to perform a repeatability study. The test condition outlined in Chapter 5, 1800 rpm and 61 ft-lb torque and at a fuel injection timing of 7° BTDC, was used for the study. As shown in Table 3.4, the study was performed over three days, with the test data being collected between 10 am and 12 pm (noon) on the various days. The intake air temperatures were within 2 degrees over the tests. The average speed was recorded within 3 rpm for a series of 60 data points. The load was recorded within 0.09 ft lbs for the same series of 60 data points.

Table 3.4: Repeatability Study Engine Test Data: 1800 rpm and 61 ft-lb torque and at a fuel injection timing of 7° BTDC

<table>
<thead>
<tr>
<th>Date</th>
<th>Time</th>
<th>Speed (rpm)</th>
<th>Load (ft-lbs)</th>
<th>Exhaust Temp (°C)</th>
<th>Boost Air Temp (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/6/2007</td>
<td>11:53 AM</td>
<td>1801.6</td>
<td>60.91</td>
<td>287.9</td>
<td>27.3</td>
</tr>
<tr>
<td>11/8/2007</td>
<td>10:22 AM</td>
<td>1800.8</td>
<td>60.89</td>
<td>285.8</td>
<td>27.6</td>
</tr>
<tr>
<td>10/9/2007</td>
<td>11:05 AM</td>
<td>1802.5</td>
<td>60.96</td>
<td>277.5</td>
<td>25.5</td>
</tr>
</tbody>
</table>

The data for the tests is shown below in Table 3.5. The emissions data error was computed to determine standard deviations for a series of 60 data points. With the standard deviation and average, the error bars were computed to be within a range of 1 to 2 % for the emissions data.

Table 3.5: Repeatability Study Test Emissions Data: 1800 rpm and 61 ft-lb torque and at a fuel injection timing of 7° BTDC

<table>
<thead>
<tr>
<th>Date</th>
<th>BSFC (g/kWh)</th>
<th>BSEC (MJ/kWh)</th>
<th>CO₂ (g/kWh)</th>
<th>CO (g/kWh)</th>
<th>NOx (g/kWh)</th>
<th>Hydrocarbons (g/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>11/6/2007</td>
<td>241.84</td>
<td>11.07</td>
<td>908.13</td>
<td>3.18</td>
<td>5.41</td>
<td>1221.19</td>
</tr>
<tr>
<td>11/8/2007</td>
<td>243.73</td>
<td>11.15</td>
<td>907.26</td>
<td>3.07</td>
<td>5.30</td>
<td>1005.90</td>
</tr>
<tr>
<td>10/9/2007</td>
<td>237.54</td>
<td>10.87</td>
<td>913.78</td>
<td>3.71</td>
<td>5.10</td>
<td>1248.15</td>
</tr>
</tbody>
</table>
The NOx (g/kWh) data for the tests is shown in Figure 2.1 with error bars. The variation between the data points shows a 5.7% difference over the three days.

Figure 3.5: Repeatability Study Test NOx (g/kWh) Emissions Data: 1800 rpm and 61 ft-lb torque and at a fuel injection timing of 7° BTDC
4.1 Preface

This chapter presents some new data and some previously published data from two American Chemical Society pre-prints [178, 179]. The initial project began with the assignment of a team of students from the class Fuel Science 504: Problems in Fuels Engineering to address the biodiesel NOx effect. The author has extended the research by finding a commercial hydrogenated biodiesel fuel and performing a series of engine tests and fuel property tests with the fuel. There were several contributing authors to the current body of work. The author’s contributions to this work include the engine tests and the viscosity tests. Stephen R. Kirby contributed by measuring the derived cetane number in the Ignition Quality Tester and the calorific values of the fuels. José Rodríguez-Fernández contributed by performing the Cloud Point and Pour Point tests. A hydrogenated biodiesel fuel has a lower iodine value and is more saturated, and thus has a different percentage of the chemical compounds than would normally be found in soy-based biodiesel. In the tests, the fuel properties of the hydrogenated biodiesel are compared neat and in blends to the normal soy based biodiesel. The engine tests involve fixing certain engine parameters to study their effect on the production of NOx from the combustion of the fuel.
4.2 Introduction

Biodiesel is an alternative diesel fuel created by the conversion of oils, fats and fatty acids to methyl and ethyl esters via esterification processes [95]. A variety of vegetable oils, typically soybean oil in the United States, and animal fats provide the source of the triglyceride fats and oils [96]. Continuous feedstock growth and livestock production provide a constant supply of source material allowing biodiesel to be a renewable source of fuel, which can be created domestically.

Additionally, biodiesel is miscible with petroleum-based diesel and works in any diesel engine with little or no modifications as pure biodiesel or as a blend with any other diesel fuel. But, the Engine Manufacturers Association recommends no more than 5% blends of biodiesel[180]. Biodiesel is a cleaner burning fuel and reduces most harmful emissions such as particulate matter, unburned hydrocarbons and carbon monoxide [53, 98].

However, a few issues need to be resolved before biodiesel fuels can be a prominent alternative fuel. The economics of providing an appropriate source material and of producing an affordable final product to create acceptable biodiesel fuels must be favorable. At present, there are significant quality control issues in the biodiesel industry[181-183]. Moreover, engine emissions of oxides of nitrogen typically increase when using biodiesel fuels [53].

One approach to combat this “biodiesel NOx effect” is to increase the degree of saturation of the ester molecules contained in the biodiesel. This degree of saturation is measured as the iodine value of the fuel. This report investigates a potential option that
may be used to achieve a higher degree of saturation: hydrogenation of soybean oil prior to transesterification of the biodiesel fuel. This research explored the approach of achieving a more saturated biodiesel fuel and observing its effects on NOx emissions in various fuel blends. A hydrogenated soy methyl ester was mixed with an ultra low sulfur diesel fuel and tested in a light duty diesel engine. This hydrogenated fuel has a higher percentage of oleic acid methyl ester, and a reduction in the linoleic and linolenic methyl esters (yielding a fuel similar to that studied by Szybist et al. [119]). Previous engine and emissions testing on a light duty diesel engine revealed decreased NOx levels for some engine modes and an increase for other modes [178, 179].

4.3 Background

4.3.1 Biodiesel Processing

Vegetable oils and animal fats are mostly made up of triacylglycerols (TAG), which are often referred to as triglycerides. The TAG are esters of fatty acids with glycerol as the backbone of the structure [184]. The fatty acids contained in the oil vary in the length of the carbon chains, as well as the number of unsaturated (double) bonds [185]. In order to be used as a diesel substitute, the vegetable oil triglycerides must be converted to methyl or ethyl esters. This is accomplished through the process of transesterification [185]. In the transesterification process, the oil is reacted with a catalyst and an alcohol (usually methanol) to form the ester groups (usually methyl
esters) from the fatty acids that are found in the original oil[184]. Glycerine is a byproduct of this reaction and must be removed before the material can be used as a fuel.

4.3.2 Hydrogenation Processing

Hydrogenation is, “the addition of hydrogen to a double or triple bond to yield a saturated product” [65]. This option of saturation of the molecules is particularly attractive as the process of hydrogenation is already being conducted on an industrial scale and is a well established technology for edible fats and oils processing. The reasons to hydrogenate a fat or oil are to change the physical form for functionality use, or to improve the oxidative stability [186]. The typical analytical evaluations for control of a hydrogenation batch are refractive index, iodine value, and melting points [186]. For this project, hydrogenated soy methyl ester was available commercially and was used in the engine testing.

According to the supplier of the hydrogenated biodiesel, the product is made by the typical hydrogenation process. Once at their facility, the further change the product by the following process. Refined and bleached (RB) soybean oil is purchased from their supplier. The RB process is aimed primarily at removing the impurities that come in with the crude vegetable oils. Then, the RB soybean oil is combined with methanol and sodium methoxide (catalyst) in a reactor/settler that allows glycerine to settle out. The processor drives the reaction through the addition of excess methanol and removal of glycerine. The crude methyl ester is flashed to remove excess methanol, washed with water to remove soap, catalyst, glycerin, and methanol. There is a final drying stage to
remove any water and methanol that is left over. Finally, atypical to the industry, the processor distills the product to create a water white methyl ester product, separating it from heavy impurities such as un-reacted glycerides [187].

Table 4.1 lists the chemical properties of a hydrogenated soy biodiesel used in the previous research [179] and this study. The fuel reports are also found in Appendix E. It is important to note the shift in the methyl oleate (C18-1) composition of the fuel from a typical soy methyl ester.

Table 4.1: Chemical properties of and Fatty Acid content of the Hydrogenated Soy Biodiesel (GCMS from supplier)

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>% C12</td>
<td>0.0</td>
</tr>
<tr>
<td>% C14</td>
<td>0.0</td>
</tr>
<tr>
<td>% C16</td>
<td>12.3</td>
</tr>
<tr>
<td>% C18</td>
<td>87.2</td>
</tr>
<tr>
<td>Iodine Value</td>
<td>90</td>
</tr>
<tr>
<td>Methanol</td>
<td>0.0</td>
</tr>
<tr>
<td>Acid Value</td>
<td>0.14</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>GC Compound</th>
<th>% Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>C16</td>
<td>12.31%</td>
</tr>
<tr>
<td>C18</td>
<td>7.81%</td>
</tr>
<tr>
<td>C18-1</td>
<td>58.17%</td>
</tr>
<tr>
<td>C18-2</td>
<td>20.24%</td>
</tr>
<tr>
<td>C18-3</td>
<td>0.92%</td>
</tr>
<tr>
<td>C22</td>
<td>0.53%</td>
</tr>
</tbody>
</table>
4.3.3 Iodine Value and NOx Emissions

Iodine Value is an analytical technique used to measure the amount of unsaturated fatty acids present in an oil. The Iodine Value, according to AOCS Method Cd 1-25, is obtained by reacting a fat with a known amount of halogen, iodine, or iodine chloride [186]. Through the reduction of the excess halogen with KOH and titration with a standard sodium thiosulfate using a starch solution as the indicator of the free iodine, the amount of iodine consumed by the fat is determined [186]. The final value is represented as the percent of iodine absorbed. A higher number means that a higher degree of unsaturated fatty acids are present [186].

According to Figure 4.1 from McCormick and coworkers [99], as the iodine value of the fuel decreases, the NOx level will decrease as well. Biodiesel from soy typically gives an Iodine Value of 130. Since the hydrogenated biodiesel has an iodine value of 90, there should be less NOx emissions from the engine in grams NOx per gram horsepower-hour. Diesel fuel is typically given an iodine value of 10.
4.4 Initial Experimental Tests and Data

The intent of the project is to decrease the NOx emissions from biodiesel combustion through the saturation of the biodiesel methyl esters, specifically methyl esters made from soybean oil. Data previously reported by the author involved the use of an ultra low sulfur diesel (ULSD) (British Petroleum 15ppm sulfur content fuel- BP15) as the base fuel and the hydrogenated soy methyl ester was blended at 50 vol% (B50)[179]. The data was collected from a Detroit Diesel Corporation (DDC) 2.5L 4-cylinder turbodiesel engine, configured with a Bosch common rail fuel injection system.

The fuel injection strategy is comprised of a pre-injection followed by a main injection to reduce emissions and engine noise. For these tests, the engine was allowed to operate as it was calibrated for normal vehicle operation. The experimental tests
followed the prescribed AVL 8-mode testing conditions as outlined in Table 4.2 below for this particular engine.

<table>
<thead>
<tr>
<th>Mode</th>
<th>Speed (rpm)</th>
<th>Load (ft-lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1000</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>1330</td>
<td>51.7</td>
</tr>
<tr>
<td>3</td>
<td>1630</td>
<td>148.7</td>
</tr>
<tr>
<td>4</td>
<td>1960</td>
<td>210.5</td>
</tr>
<tr>
<td>5</td>
<td>4000</td>
<td>39.8</td>
</tr>
<tr>
<td>6</td>
<td>3850</td>
<td>91.5</td>
</tr>
<tr>
<td>7</td>
<td>3850</td>
<td>157.8</td>
</tr>
<tr>
<td>8</td>
<td>3670</td>
<td>224.2</td>
</tr>
</tbody>
</table>

Based on the data presented in Figure 4.2, there is a NOx reduction for 5 of the 8 modes for this particular engine. However, there is an increase in NOx for the three low speed modes for the engine, which is where the engine might operate for 1/3 of the time, in a typical duty cycle for a light duty vehicle.

Figure 4.2: NOx (g/kg fuel) vs AVL 8 mode test. [179]
The Brake Specific Fuel Consumption (BSFC), shown in Figure 4.3, is higher for the biodiesel blend due to the decrease of the lower heating value from the biodiesel portion of the fuel. Therefore, the engine required more fuel to achieve the speed and load condition.

![BSFC (g/kWh) vs AVL 8 mode test](image)

**Figure 4.3:** BSFC (g/kWh) vs AVL 8 mode test [179]

There is an increase in CO emissions which is not consistent across the modes, presented in Figure 4.4. At high speeds, this difference becomes small between the fuels.
The data collected was an average of two data points for each fuel, which is insufficient to obtain a measure of the statistical significance of the results. Additionally, the engine was not equipped at the time with the ability to collect pressure traces which would enhance the analysis to include the ignition delay of the fuels, as well as the effect of the pilot and main injections on the heat release.

After reviewing this initial data, a significant change in NOx emissions was not observed as expected. It was concluded that the effect of the EGR and of the injection timing may be impacting the outcome. Therefore, another set of engine tests was performed to study the impact of the blending of the fuel on the NOx emissions, without the use of EGR. This second study was conducted to gather more information about how the engine’s fuel injection system was operating, and to gather pressure traces and heat release information. The set of experiments involved running the engine at the lower
speeds and loads and varying the blend levels of both the hydrogenated biodiesel and a conventional soy based biodiesel.

4.5 Second Set of Experimental Tests

A set of engine tests was performed with the hydrogenated biodiesel fuels, to compare to a conventional biodiesel fuel. The tests were performed with no engine EGR, but with the normal pilot and main fuel injection pulse, but not held to a fixed timing via the INCA/ETAS system. Fuel property tests were also conducted.

Engine conditions for this set of tests were limited due to complications with the engine driveshaft. Although the goal was to span engine speed and load while using the engine as it was normally programmed to operate, that was not possible. The test conditions are shown in Table 4.3. Four engine modes were tested, with no EGR applied and with the normal pilot and main fuel injection pulse. Emissions data and TEOM PM data were collected. The emission data was collected through a labview program that was connected to the AVL CEB II. The engine operating data was collected with a Leeds & Northrup MicroMax data system.

Table 4.3: DDC 2.5L Engine Test Specification

<table>
<thead>
<tr>
<th>Mode Number</th>
<th>Speed (rpm)</th>
<th>Load (ft-lbs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1500</td>
<td>50</td>
</tr>
<tr>
<td>2</td>
<td>1500</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td>1660</td>
<td>75</td>
</tr>
<tr>
<td>4</td>
<td>1660</td>
<td>125</td>
</tr>
</tbody>
</table>
4.6 Fuel Property Tests and Results

To understand the physical changes that arise in the fuel based on a change in the chemical composition of the fuel (in this case via the hydrogenation of the fuel), some tests were conducted on the fuels to identify the change in properties. The tests and the results are described in the following sections. When the normal biodiesel fuel is shown in a table, a capital B is used. For the hydrogenated biodiesel, a capital H is used. When the biodiesel is mixed with the diesel fuel in a blended amount, the amount is designated by a number following the capital letter. For example, B20 represents 20% conventional biodiesel blended in diesel fuel.

4.6.1 Cetane number by Ignition Quality Tester (IQT)

The derived cetane number (DCN) for each of the fuel blends was measured in accordance with ASTM D6890-07a [188]. A correlation has been developed to convert the measured ignition delay into a DCN, which is correlated with the CN measured by ASTM D613 (CFR Cetane Rating engine). The ignition delay (defined as the elapsed time from injection to where the chamber pressure reaches $P_{\text{initial}} + 50$ psi) under specified conditions is measured using the Ignition Quality Tester (IQT). The instrument also calculates a standard deviation of the derived cetane number based on the number of sample repetitions. The instrument is shown in Figure 4.5. The system is fully automated and an experiment consists of 15 pre-injections (to equilibrate system temperatures) followed by 32 injections. The reported DCNs are the averages of these 32 injections of pre-filtered fuels. A sample of data from a single injection is presented as a
screen shot in Figure 4.6. Table 4.4 shows the cetane number for the fuels based on ASTM D6890-07a. As is shown in the table, the biodiesel fuel has a higher cetane number and thus a shorter ignition delay. The hydrogenated biodiesel has a higher cetane number than the normal soy-based biodiesel. Knothe and coworkers showed the cetane number associated with the specific fatty acid chain lengths [101]. Thus, an increase in the methyl oleate composition of the biodiesel fuel will increase the cetane number. In previous work, Knothe coworkers also showed that the pre-combustion compounds formed with unsaturated fatty compounds had a lower cetane number, thus explaining the low cetane number for unsaturated biodiesel fuels [189].

Figure 4.5: Photograph of the Ignition Quality Tester (IQT) at the Penn State Energy Institute
Figure 4.6: Sample data readout from the IQT. Needle lift is displayed in yellow and combustion pressure in blue.

Table 4.4: Derived Cetane Number (DCN)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ignition Delay (ms)</th>
<th>DCN</th>
<th>Standard Deviation of DCN</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD (BP15)</td>
<td>4.231</td>
<td>47.0</td>
<td>0.85</td>
</tr>
<tr>
<td>B20</td>
<td>4.106</td>
<td>48.4</td>
<td>1.09</td>
</tr>
<tr>
<td>B40</td>
<td>3.983</td>
<td>49.9</td>
<td>1.26</td>
</tr>
<tr>
<td>B100</td>
<td>3.907</td>
<td>50.8</td>
<td>1.97</td>
</tr>
<tr>
<td>H20</td>
<td>3.888</td>
<td>51.1</td>
<td>1.07</td>
</tr>
<tr>
<td>H40</td>
<td>3.726</td>
<td>53.3</td>
<td>0.96</td>
</tr>
<tr>
<td>H100</td>
<td>3.114</td>
<td>65.1</td>
<td>2.25</td>
</tr>
<tr>
<td>B100- same batch/ different barrel</td>
<td>3.723</td>
<td>53.4</td>
<td>2.16</td>
</tr>
</tbody>
</table>
4.6.2 Compound analysis

The hydrogenated biodiesel was analyzed with GCMS method by the company supplying the sample. The data is used to gain information on the compound composition of the fuel. The biodiesel from AGP was analyzed by the USDA Agricultural Research Service with a similar GCMS method [190]. The reports are provided in Appendix E. The sample reports from AGP are also provided in Appendix E.

4.6.3 Cloud Point and Pour Point

Cloud Point and Pour Point tests are described by ASTM D 2500-99 and D 97-96a, respectively [191, 192]. The intent of the tests was to evaluate the cloud and pour point of the fuels according to ASTM D 2500-99 and D 97-96a, but that was impossible because of the available equipment. Just as ASTM rules show, different baths would have been necessary at 0, -18, -33, … °C, but only one was available [191, 192]. In addition, the lowest temperature reached, even with two external coolers, was only -24 °C, so it was necessary to place the test jars directly into the cooling medium to perform the tests.

Raw numbers observed for Cloud Point (CP) and Pour Point (PP) are shown in Table 4.5. Pour Point is plotted in Figure 4.7 by fuel type. Cloud Point is plotted by fuel in Figure 4.8. Each sample was tested twice, and the identical values were measured. One of the major problems associated with biodiesel is the low cloud point and pour point [102]. Therefore, it is important to know the effect of the saturation on these properties. As can be seen, both cloud and pour point increase with increasing percentage of biodiesel in the fuel, either with normal biodiesel or hydrogenated
biodiesel. The more saturated hydrogenated biodiesel showed higher cloud and pour points (poorer cold flow properties) as it is widely reported in the literature [193, 194].

Table 4.5: Cloud Point and Pour Point

<table>
<thead>
<tr>
<th></th>
<th>ULSD (BP15)</th>
<th>B20</th>
<th>H20</th>
<th>B40</th>
<th>H40</th>
<th>B100</th>
<th>H100</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Cloud Point (°C)</strong></td>
<td>-12</td>
<td>-10</td>
<td>-10</td>
<td>-9</td>
<td>-8</td>
<td>0</td>
<td>5</td>
</tr>
<tr>
<td><strong>Pour Point (°C)</strong></td>
<td>-21</td>
<td>-18</td>
<td>-12</td>
<td>-12</td>
<td>-12</td>
<td>-6</td>
<td>0</td>
</tr>
</tbody>
</table>

Figure 4.7: Pour Point (°C) by fuel type (B percentage is the blend percentage in the fuel)
4.6.4 Viscosity

Viscosity is determined by using a timed method through the use of a capillary viscometers described in ASTM D 446-07 [195]. The procedure is described in ASTM D 445-06 [196]. A Modified Oswald Viscometer was used, numbered R201. For these tests, the fluid was placed in the viscometer bath set at 40° C for 30 minutes before the timed test. A sample size of 10-15 measurements were collected and averaged. The data is shown below in Table 4.6. As shown by Knothe and coworkers, the kinematic viscosity of methyl esters is higher than petroleum diesel fuel, and the viscosity increases
as the C18 molecule becomes more saturated [102, 197]. Thus, the hydrogenated biodiesel fuel will have a higher viscosity than the conventional soy-based biodiesel.

Table 4.6: Viscosity (cSt) for the various fuels and blends at (40°C)

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Viscosity (cSt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD (BP15)</td>
<td>2.52</td>
</tr>
<tr>
<td>B20</td>
<td>2.68</td>
</tr>
<tr>
<td>B100</td>
<td>3.96</td>
</tr>
<tr>
<td>H20</td>
<td>2.80</td>
</tr>
<tr>
<td>H100</td>
<td>4.61</td>
</tr>
</tbody>
</table>

4.6.5 Higher Heating Value

This test is performed per ASTM D5865-07 and is used to determine the calorific value of the component with a bomb calorimeter [198]. The results of the tests of the fuels are shown in Table 4.7. As in seen in the table, the heating value of the two biodiesel fuels is less than that of the diesel. The heating value of the hydrogenated biodiesel is slightly higher than for the conventional biodiesel as a result of the saturation. Knothe shows in his work that the heating value for methyl oleate is higher than the heating value for methyl linoleate and methyl linolenate [102]. Even with a change in the chemical composition of the biodiesel fuels, they have similar heating values.
4.6.6 Boiling Range Distribution

The test for boiling range distribution is performed per ASTM D 2887 [199]. The boiling range distribution of petroleum fractions are determined by Gas Chromatography. The test is limited to samples with a boiling range greater than 55 °C and a final boiling point of 538 °C, and having a vapor pressure sufficiently low to permit sampling at ambient temperatures. The three neat fuels boiling ranges were tested, and the results are shown in Table 3.2. Boiling range distribution provides information about the volatility of the fuel, and particular end points have shown trends with exhaust emissions, as for example T90 has trended with particulate matter mass. As is shown in the table, the range for the ULSD is much broader than for the biodiesel fuels. The two biodiesel fuels have similar boiling ranges.

<table>
<thead>
<tr>
<th>Fuel</th>
<th>Calorific Value (Btu/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ULSD (BP15)</td>
<td>19671</td>
</tr>
<tr>
<td>B20</td>
<td>19177</td>
</tr>
<tr>
<td>B40</td>
<td>18615</td>
</tr>
<tr>
<td>B100</td>
<td>17115</td>
</tr>
<tr>
<td>H20</td>
<td>19200</td>
</tr>
<tr>
<td>H40</td>
<td>18715</td>
</tr>
<tr>
<td>H100</td>
<td>17138</td>
</tr>
</tbody>
</table>
4.7 Engine Tests Results and Data Analysis

The following sections show the data that has been analyzed and plotted. The set of tests involve examination of the fuel blends being over various engine speeds and loads without EGR.

Table 4.8: Boiling Range Distribution (°C) of the Fuels

<table>
<thead>
<tr>
<th>% Off</th>
<th>ULSD (BP15) BP(°C)</th>
<th>B100 BP(°C)</th>
<th>H100 BP(°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>IBP</td>
<td>115.0</td>
<td>326.9</td>
<td>326.4</td>
</tr>
<tr>
<td>5</td>
<td>165.3</td>
<td>328.3</td>
<td>327.9</td>
</tr>
<tr>
<td>10</td>
<td>184.7</td>
<td>333.3</td>
<td>328.9</td>
</tr>
<tr>
<td>15</td>
<td>198.5</td>
<td>350.3</td>
<td>350.1</td>
</tr>
<tr>
<td>20</td>
<td>210.9</td>
<td>350.9</td>
<td>350.9</td>
</tr>
<tr>
<td>25</td>
<td>220.7</td>
<td>351.3</td>
<td>351.5</td>
</tr>
<tr>
<td>30</td>
<td>230.8</td>
<td>351.6</td>
<td>351.9</td>
</tr>
<tr>
<td>35</td>
<td>239.4</td>
<td>351.9</td>
<td>352.3</td>
</tr>
<tr>
<td>40</td>
<td>249.3</td>
<td>352.1</td>
<td>352.6</td>
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<tr>
<td>45</td>
<td>257.5</td>
<td>352.3</td>
<td>352.9</td>
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<tr>
<td>50</td>
<td>266.7</td>
<td>352.5</td>
<td>353.2</td>
</tr>
<tr>
<td>55</td>
<td>275.6</td>
<td>352.7</td>
<td>353.4</td>
</tr>
<tr>
<td>60</td>
<td>285.1</td>
<td>352.9</td>
<td>353.7</td>
</tr>
<tr>
<td>65</td>
<td>293.6</td>
<td>353.1</td>
<td>353.9</td>
</tr>
<tr>
<td>70</td>
<td>301.0</td>
<td>353.3</td>
<td>354.1</td>
</tr>
<tr>
<td>75</td>
<td>311.7</td>
<td>353.4</td>
<td>354.4</td>
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<tr>
<td>80</td>
<td>321.2</td>
<td>353.6</td>
<td>354.6</td>
</tr>
<tr>
<td>85</td>
<td>333.1</td>
<td>353.8</td>
<td>354.9</td>
</tr>
<tr>
<td>90</td>
<td>348.3</td>
<td>354.0</td>
<td>355.3</td>
</tr>
<tr>
<td>95</td>
<td>368.3</td>
<td>354.8</td>
<td>355.9</td>
</tr>
<tr>
<td>FBP</td>
<td>429.0</td>
<td>360.6</td>
<td>361.4</td>
</tr>
</tbody>
</table>
4.7.1 Fuel Tests over various Engine Modes

The set of data represents the fuels and their blends being tested over various engine modes. Gaseous emissions and particulate matter data were collected. Emissions results are shown in Figure 4.9 - Figure 4.12. Fuel consumption results are shown in Figure 4.13 - Figure 4.15. Exhaust Temperatures are shown in Figure 4.16.

As shown in Figure 4.9 and detailed in previous literature, NOx increases with the addition of 20% soy-based biodiesel to the diesel fuel in comparison to the conventional diesel fuel. Over the various modes, the increase in NOx emissions is different: Mode 1-20.2 % increase, Mode 2- 4.6 % increase, Mode 3- 2.3 % increase, and Mode 4- 10.8 % increase. However, previous research has suggested a 1% increase in NOx emissions for a 10% increase in biodiesel blended in diesel fuel [53]. The data in this research with a light duty diesel engine refutes the given general trend for heavy duty diesel engines over the past 40 years collected in older engine equipment and in various engine test cycles.

As shown in this research and by other researchers, the NOx emissions increase with load, as shown quite clearly in Modes 2 and 4 in comparison to Modes 1 and 3[122, 200]. Therefore, it is clear that the general trend with biodiesel and NOx emissions does not take into account the change in engine testing conditions and engine equipment, although this new data suggests that it does not adequately represent the trend.

This data also shows a difference in the NOx data shown by Zhang in his work with the same engine and with a B40 blend. Mode 3 is the comparable point. Zhang showed that with the B40 blend, there was a slight reduction in NOx emissions (brake specific – g/kWh) with the double injection strategy [121]. However, the injection
strategy in this research, as shown later in the needle lift data, was different. The pilot injection was not as advanced as in Zhang’s research [121]. This indicates that phasing of the pilot injection to the main injection can have some significant impact on NOx emissions.

For the 40% soy-based biodiesel addition, a decrease in NOx emissions over conventional diesel was observed: Mode 1- 11.7% decrease, Mode 2- 13.8 % decrease, Mode 3- 14.3% decrease, Mode 4- 3.3% decrease. As suggested by the literature, hydrogenated biodiesel gives lower NOx emissions [99], and that is shown in this data set. The addition of 20% and 40% of the hydrogenated biodiesel fuel gave similar NOx emissions, and these were similar to the 40% soy-based biodiesel. At this point, there are two explanations that are apparent: 1) there is some change in the chemistry of the fuels with the B40 and then H20 and H40 blends that reduced the NOx emissions, and 2) this change in fuel chemistry along with the injection strategy of pilot and main timing led to this decrease.
CO\textsubscript{2} emissions are shown in Figure 4.10. The data for all 4 modes show CO\textsubscript{2} emissions in the approximate same range taking into account the error bars. Mode 1 shows an increase of 4.7\% in the CO\textsubscript{2} emissions for B20 with a decrease of 6.5 \% for B40 in comparison to the baseline diesel fuel. The H20 and H40 are similar to the baseline diesel, showing a decrease of .8 \% and 3.1\% respectively. Mode 2 shows a similar trend as Mode 1. Mode 3 shows relatively the same CO\textsubscript{2} emissions for all fuels. Mode 4 shows an increase in CO\textsubscript{2} emissions for the biodiesel fuels, with B20 an 8.3\% increase, B40 an 8\% increase, H20 a 7.8\% increase, and H40 a 4.5\% increase.
Hydrocarbon emissions are shown in Figure 4.11. As shown in the figure, hydrocarbon emissions decrease with increasing load. Also, shown in all modes, but more pronounced in Mode 1, as the biodiesel blend is increased from 20 to 40 %, the hydrocarbon emissions decrease. The hydrogenated biodiesel gives a reduction of hydrocarbons over all modes, and with the increasing % of blend in the baseline diesel. For the H20 blend, the percent reduction in hydrocarbons in comparison to the conventional diesel fuel are: Mode 1- 35.6%, Mode 2- 29.6%, Mode 3- 22.3%, Mode 4- 23.6%.
Figure 4.11: Hydrocarbon Emissions (g/kg fuel) for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, Mode 2= 1500 rpm/100 ft-lb, Mode 3= 1660 rpm/75 ft-lb, Mode 4= 1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

CO emissions are shown in Figure 4.12. For Mode 1, an increase of 4.8% in CO is seen for the B20 blend, but decreases shown for all other biodiesel blends: B40 – 1.0%, H20-6.5%, and H40-9.7%. For Mode 2, a decrease is shown for all biodiesel blends: B20 – 7.1%, B40 - 12.0%, H20 – 9.3%, and H40 – 17.2%. For Mode 3, an increase of 1.0 % in CO is seen for the B40 blend, but decreases shown for all other biodiesel blends: B20 - 4.8%, H20 - 8.6%, and H40 - 12.3%. For Mode 4, a decrease is shown for all biodiesel blends: B20- .7%, B40 - 4.6%, H20 - 6.1%, and H40 - 12.9%.
Fuel consumption is shown in Figure 4.13. As shown in the data, the fuel consumption error bars make it difficult to determine a change in the actual consumption. However, it would be expected that as the soy-based biodiesel and hydrogenated biodiesel are blended into diesel fuel, more fuel would be required since the calorific values of both fuels are lower than diesel. It should also be noted that the fuel injector delivery operates on a volume fuel injection, and the density of the soy-based biodiesel and hydrogenated biodiesel are similar, and higher than the convention diesel fuel. Therefore, as the engine would need to adjust to inject more of the biodiesel fuel to compensate for the lower calorific value, it would also be adjusting to deliver less volume to compensate for the change in density. Table 4.9 shows the percent change in fuel consumption (g/hr) in comparison to conventional diesel fuel.
Brake Specific Fuel Consumption (BSFC) is shown in Figure 4.14. The fuel consumption based on the power delivery by the engine shows that slightly more hydrogenated biodiesel was needed for Mode 1 and 2, but approximately the same for the other modes. The engine required the same soy-based biodiesel in comparison to the baseline diesel fuel for all 4 modes. Table 4.9 shows the percent change in BSFC (g/kWh) in comparison to conventional diesel fuel.
Figure 4.14: Brake Specific Fuel Consumption (g/kWh) for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, Mode 2= 1500 rpm/100 ft-lb, Mode 3= 1660 rpm/75 ft-lb, Mode 4= 1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Brake Specific Energy Consumption (BSEC) is shown in Figure 4.15. This figure is based on the heating value of the fuel divided by the power output from the engine for the particular fuel. Mode 1 and 2 show that more hydrogenated biodiesel is required for the same power output, but that the soy-based biodiesel and baseline fuels are relatively similar. The Mode 1 soy-based biodiesel requirement for less fuel is not consistent with what would have been expected. For Mode 3 and 4, the energy equivalent basis shows

<table>
<thead>
<tr>
<th></th>
<th>Fuel (g/hr)</th>
<th>BSFC (g/kWh)</th>
<th>BSEC (MJ/kWh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>b20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m1</td>
<td>-6.1</td>
<td>-6.1</td>
<td>-8.5</td>
</tr>
<tr>
<td>m2</td>
<td>0.6</td>
<td>0.6</td>
<td>-1.9</td>
</tr>
<tr>
<td>m3</td>
<td>1.0</td>
<td>1.0</td>
<td>-1.6</td>
</tr>
<tr>
<td>m4</td>
<td>-1.4</td>
<td>-1.4</td>
<td>-3.9</td>
</tr>
<tr>
<td>b40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m1</td>
<td>6.8</td>
<td>6.8</td>
<td>1.1</td>
</tr>
<tr>
<td>m2</td>
<td>6.7</td>
<td>6.7</td>
<td>0.9</td>
</tr>
<tr>
<td>m3</td>
<td>-1.7</td>
<td>-1.7</td>
<td>-7.0</td>
</tr>
<tr>
<td>m4</td>
<td>-0.1</td>
<td>-0.1</td>
<td>-5.5</td>
</tr>
<tr>
<td>h20</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m1</td>
<td>-2.5</td>
<td>-2.5</td>
<td>-4.8</td>
</tr>
<tr>
<td>m2</td>
<td>2.0</td>
<td>2.0</td>
<td>-0.5</td>
</tr>
<tr>
<td>m3</td>
<td>-0.9</td>
<td>-0.9</td>
<td>-3.3</td>
</tr>
<tr>
<td>m4</td>
<td>-1.3</td>
<td>-1.3</td>
<td>-3.7</td>
</tr>
<tr>
<td>h40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m1</td>
<td>2.3</td>
<td>2.3</td>
<td>-2.7</td>
</tr>
<tr>
<td>m2</td>
<td>6.0</td>
<td>6.0</td>
<td>0.8</td>
</tr>
<tr>
<td>m3</td>
<td>1.1</td>
<td>1.1</td>
<td>-3.8</td>
</tr>
<tr>
<td>m4</td>
<td>1.6</td>
<td>1.6</td>
<td>-3.4</td>
</tr>
</tbody>
</table>

Table 4.9: Percent Change in Emissions in Comparison to Conventional Diesel fuel for Fuel Consumption (g/hr), Brake Specific Fuel Consumption (g/kWh), and Brake Specific Energy Consumption (MJ/kWh)
the same fuel requirement for each fuel compared. Again, this would not be expected since the fuels for this figure are adjusted for the difference in calorific value of the fuel. Table 4.9 shows the percent change in BSEC (MJ/kWh) in comparison to conventional diesel fuel.

Figure 4.15: Brake Specific Energy Consumption (MJ/kWh) for DDC 2.5L engine, Mode 1 = 1500 rpm/50 ft-lb, Mode 2 = 1500 rpm/100 ft-lb, Mode 3 = 1660 rpm/75 ft-lb, Mode 4 = 1660 rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

Exhaust temperatures for each fuel are shown in Figure 4.16. These are downstream exhaust temperatures taken at the same exhaust point for each test. As shown in the figure, Mode 1 shows an increase in the exhaust temperature for each biodiesel fuel blend, and with a slight increase for the 40% blend. Mode 2 shows an
increase in the temperature for the B40, H20, and H40 blends. In Mode 3 and 4, the exhaust temperature is the same or slightly above the baseline diesel temperature for the soy-based biodiesel, but a definite increase is shown for the hydrogenated blends.

Figure 4.16: Exhaust Temperature (°C) for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, Mode 2= 1500 rpm/100 ft-lb, Mode 3= 1660 rpm/75 ft-lb, Mode 4= 1660 rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

4.7.2 Pressure Trace and Heat Release Analysis

The following figures show the pressure trace and heat release analysis from the testing. A set of 200 pressure cycles were collected for each cylinder. In this group of figures, the data from cylinder 3 is represented as an averaged cycle from the 200 traces.
Pressure trace data from Mode 1 for the test fuels are shown in Figure 4.17. The plot shows similar pressure curves for each fuel. The premixed and diffusion phases are pronounced and distinct in the plot. Table 4.10 shows the maximum pressure achieved by each fuel.

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Pressure (bar)</td>
<td>55.9</td>
<td>55.7</td>
<td>54.9</td>
<td>54.7</td>
<td>54.3</td>
</tr>
</tbody>
</table>
Pressure trace data from Mode 2 for the test fuels are shown in Figure 4.18. The plot shows similar pressure curves for each fuel. The premixed and diffusion phases are pronounced and distinct in the plot. Table 4.11 shows the maximum pressure achieved by each fuel.

![Figure 4.17: Mode 1 Pressure Trace Plot for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)](image)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Maximum Pressure (bar)</strong></td>
<td>67.0</td>
<td>66.4</td>
<td>64.9</td>
<td>65.4</td>
<td>65.1</td>
</tr>
</tbody>
</table>
Pressure trace data from Mode 3 for the test fuels are shown in Figure 4.19. The plot shows similar pressure curves for each fuel. The premixed and diffusion phases are pronounced and distinct in the plot. Table 4.12 shows the maximum pressure achieved by each fuel.
Table 4.12: Mode 3 Maximum Pressure (bar)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Pressure (bar)</td>
<td>66.0</td>
<td>65.4</td>
<td>62.9</td>
<td>63.6</td>
<td>63.4</td>
</tr>
</tbody>
</table>

Figure 4.19: Mode 3 Pressure Trace Plot for DDC 2.5L engine, Mode 3 = 1660 rpm/75 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Pressure trace data from Mode 4 for the test fuels are shown in Figure 4.20. The plot shows similar pressure curves for each fuel. The premixed and diffusion phases are pronounced and distinct in the plot. Table 4.13 shows the maximum pressure achieved by each fuel.

Table 4.13: Mode 4 Maximum Pressure (bar)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Pressure (bar)</td>
<td>75.8</td>
<td>73.9</td>
<td>72.9</td>
<td>72.7</td>
<td>72.7</td>
</tr>
</tbody>
</table>
Heat release data from Mode 1 through Mode 4 for the test fuels are shown in Figures 4.21 through 4.24. All heat release data plots show similar rate of heat release curves for each fuel in each specific mode. Based on the needle lift data plots for the pilot and main injection, the heat release data plots show a heat release for each injection pulse.

Figure 4.20: Mode 4 Pressure Trace Plot for DDC 2.5L engine, Mode 4= 1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.21: Mode 1 Rate of Heat Release Plot for DDC 2.5L engine, Mode 1 = 1500 rpm/50 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.22: Mode 2 Rate of Heat Release Plot for DDC 2.5L engine, Mode 2= 1500 rpm/100 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.23: Mode 3 Rate of Heat Release Plot for DDC 2.5L engine, Mode 3= 1660 rpm/75 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.24: Mode 4 Rate of Heat Release Plot for DDC 2.5L engine, Mode 4= 1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
4.7.3 Needle Lift

The following figures show the fuel injector needle lift analysis. A set of 200 needle lift cycles were collected for each cylinder. In this group of figures, the data from the needle lift sensor applied in cylinder 1 is represented as an averaged cycle from the 200 traces.

Needle Lift data from Mode 1 through Mode 4 for the test fuels are shown in Figures 4.25 through 4.28. The needle lift data plots show similar needle lift curves for each fuel in each specific mode.
Figure 4.25: Mode 1 Needle Lift Plot for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.26: Mode 2 Needle Lift Plot for DDC 2.5L engine, Mode 2= 1500 rpm/100 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.27: Mode 3 Needle Lift Plot for DDC 2.5L engine, Mode 3 = 1660 rpm/75 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
Figure 4.28: Mode 4 Needle Lift Plot for DDC 2.5L engine, Mode 4= 1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
4.7.4 Bulk Cylinder Temperature

The following figures show the bulk cylinder temperature analysis from the testing. A set of 200 pressure cycles were collected for each cylinder and bulk cylinder temperature was calculated. In this group of figures, the data from cylinder 3 is represented as an averaged cycle from the 200 traces.

Bulk cylinder temperature data from Mode 1 for the test fuels are shown in Figure 4.29. The plot shows similar bulk temperature for each fuel, but with varying maximum temperatures. Table 4.14 shows the maximum bulk temperature achieved. As is shown in the table, the bulk temperature is higher for the biodiesel blends than for the diesel fuel. The higher biodiesel blend does not produce a higher bulk cylinder temperature.
Figure 4.29: Mode 1 Bulk Cylinder Temperature Plot for DDC 2.5L engine, Mode 1= 1500 rpm/50 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

Table 4.14: Mode 1 Maximum Bulk Temperature (K)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Bulk Temperature (K)</td>
<td>1050.7</td>
<td>1082.9</td>
<td>1079.2</td>
<td>1079.3</td>
<td>1065.3</td>
</tr>
</tbody>
</table>
Bulk cylinder temperature data from Mode 2 for the test fuels are shown in Figure 4.30. The plot shows similar bulk temperature for each fuel, but with varying maximum temperatures. Table 4.15 shows the maximum bulk temperature achieved. As is shown in the table, the bulk temperature is higher for the biodiesel blends than for the diesel fuel. The higher biodiesel blend does produce a higher bulk cylinder temperature with all cases.
Figure 4.30: Mode 2 Bulk Cylinder Temperature Plot for DDC 2.5L engine, Mode 2 = 1500 rpm/100 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

Table 4.15: Mode 2 Maximum Bulk Temperature (K)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Bulk Temp</td>
<td>1263.6</td>
<td>1272.9</td>
<td>1273.6</td>
<td>1280</td>
<td>1292.8</td>
</tr>
</tbody>
</table>
Bulk cylinder temperature data from Mode 3 for the test fuels are shown in Figure 4.31. The plot shows similar bulk temperature for each fuel, but with varying maximum temperatures. Table 4.16 shows the maximum bulk temperature achieved. As is shown in the table, the bulk temperature is higher for the biodiesel blends than for the diesel fuel. The higher biodiesel blend does not produce a higher bulk cylinder temperature in all cases.
Figure 4.31: Mode 3 Bulk Cylinder Temperature Plot for DDC 2.5L engine, Mode 3= 1660 rpm/75 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)

Table 4.16: Mode 3 Maximum Bulk Temperature (K)

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Bulk Temperature (K)</td>
<td>1157.6</td>
<td>1179.4</td>
<td>1170.5</td>
<td>1179.5</td>
<td>1183.7</td>
</tr>
</tbody>
</table>
Bulk cylinder temperature data from Mode 4 for the test fuels are shown in Figure 4.32. The plot shows similar bulk temperature for each fuel, but with varying maximum temperatures. Table 4.17 shows the maximum bulk temperature achieved. As is shown in the table, the bulk temperature is higher for the biodiesel blends than for the diesel fuel. The higher biodiesel blend does produce a higher bulk cylinder temperature.

Figure 4.32: Mode 4 Bulk Cylinder Temperature Plot for DDC 2.5L engine, Mode 4=1660rpm/125 ft-lb, with pilot and main injection, without EGR, for various biodiesel blends in comparison to baseline diesel fuel ULSD (BP15)
4.8 Discussion

There are two aspects to the data that deserve discussion. First, the current theories for the biodiesel NOx effect will be reviewed while discussing the results of this set of experiments previously presented. The nine theories follow with a brief discussion of each in relation to the data. Second, the fuel injection strategy of this engine, with a pilot pulse and a main injection, provided an interesting set of results, but with a complicated set of mechanisms acting.

4.8.1 Discussion of Biodiesel NOx Theories

Adiabatic Flame Temperature

From a general review of the calculation for the adiabatic flame temperature, it seems that one must know the enthalpy of formation for the specific fuel. While some data on the methyl esters of biodiesel is available, there is not much data available on the specific carbon chain species that would allow an exact adiabatic flame temperature to be calculated [102]. However, a simple calculation was performed by Zhang comparing methyl oleate and a diesel surrogate fuel [201]. There is some thermophysical data

<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>bp15</th>
<th>b20</th>
<th>b40</th>
<th>h20</th>
<th>h40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum Bulk Temperature (K)</td>
<td>1314.5</td>
<td>1337.6</td>
<td>1362.7</td>
<td>1359.2</td>
<td>1374.8</td>
</tr>
</tbody>
</table>
available in the NASA CEA to make this calculation. As seen in Zhang’s results, the methyl oleate gave a lower adiabatic flame temperature for both the low load and high load conditions, and across various stoichiometries [201]. At stoichiometric conditions, the temperature difference was 20 K [201]. Zhang concluded that the adiabatic flame temperature difference could not explain the NOx emissions increase seen with biodiesel.

In comparing Zhang’s calculation to the fuel property data for this research, it should be noted that the actual NOx emissions from Zhang’s work was based on a biodiesel fuel that had about 22% methyl oleate composition, which is the same soy-based normal biodiesel used in this work. Those samples are represented as AGP#1 and AGP#2 in Appendix B. The hydrogenated biodiesel had an approximate 69% methyl oleate composition, which more closely matches the calculation variable that Zhang used, assuming 100% methyl oleate. Making this assumption, this data could explain the change seen in the reduction of the NOx for the hydrogenated biodiesel.

Ban-Weiss and coworkers suggest that the higher flame temperature for biodiesel is related to the higher flame temperature seen with molecules that have double bonds [110]. Therefore, saturated molecules will have lower flame temperatures. The hydrogenated biodiesel has 3 times more methyl oleate than the soy-based biodiesel, and as a result has a lower number of double bonded molecules. This is also a good argument for explaining the reduction in NOx shown in Figure 4.9, which is then due to a reduction in the number of double bounded molecules in the fuel composition. Table 4.18 shows the description of the methyl esters and their composition. Table 4.19 shows the change in the composition to the fuel and how this affects the carbon, hydrogen, and oxygen composition, in addition to the number of double bonds available in the fuel.
A calculation of the adiabatic flame temperature was made based on the higher heating value of the fuel to investigate whether the NOx increase with the soy based biodiesel, and the NOx decrease with the hydrogenated biodiesel could be attributed to the difference in temperature. With the available compound information for the fuels, the enthalpy of formation was calculated from the balanced stoichiometric equation for the fuel. Since the direct heat of vaporization information was not available, for simplicity,
an assumption was made that this was constant across the three fuels. With the enthalpy of formation and through the use of HP Flame, a computer tool developed by Turns [31] and based on the Olikara and Borman routines [202], the adiabatic flame temperature was determined for varying stoichiometries at a pressure of 50 bar. Figure 4.33 shows the results based on the calculations. The ULSD and the H100 trend in a similar manner, while the B100 is higher by approximately 100K at $\phi=1$. This data supports the theory that the higher NOx emissions shown for the B20 version are due to the higher adiabatic flame temperature for B100.

![Diagram: Adiabatic Flame Temperature of fuels at a pressure of 50 bar vs. Phi ($\phi$)](image)

Figure 4.33: Adiabatic Flame Temperature of fuels at a pressure of 50 bar vs. Phi ($\phi$)
The adiabatic flame temperature data presented here follows the trend shown by the modeling by Ban-Weiss and coworkers [110], that a more saturated compound will have a lower peak temperature than its comparable unsaturated compound, thus producing lower NOx emissions. Cheng and coworkers also computed adiabatic flame temperature with modified version of the EQUIL module of the CHEMKIN software package [42]. Their modified version accounts for the mixing and vaporization of the fuel at the engine coolant’s conditions at the calculated motored TDC temperature and pressure to properly account for differences in the adiabatic flame temperature due to differences in the latent heat of vaporization of the fuels. This yielded differences in the charge gas temperature after the fuels were vaporized [42]. They compared methyl oleate to a primary reference fuel for diesel for various stoichiometries and found that the adiabatic flame temperatures were the same up to $\varphi = 1.5$. Above this, the adiabatic flame temperature of the primary reference fuel was higher. And, data presented by Zhang shows that the adiabatic flame temperature of methyl oleate is lower than a surrogate diesel fuel by 20K based on modeling with the NASA CEA chemical equilibrium code [203]. The adiabatic flame temperature data for methyl oleate from Zhang, and Chen and coworkers is similar in trends to the data presented here for the adiabatic flame temperature because the H100 fuel composition is approximately 60% methyl oleate.

**Flame Radiation**

Again, the theory about soot and flame radiation claims that the reduction in soot concentration reduces the soot radiation in the flame zone and thus the diffusion flame
temperature is higher and thus thermal NOx formation increases [113, 114]. There was no data collected in this research to verify or refute this theory, although the sooting tendency of the B20 and H20 fuels should have been similar, ruling out the effect of shifts in flame radiation causing the NOx effect.

**Mixing**

Musculus showed that as the pre-mixed burn fraction increases, the NOx emissions increase [113]. The pressure traces from this research, Figures 4.17 through 4.20, show a consistent premixed and diffusion burn for each fuel and for each speed and load condition.

**Prompt NO**

Researchers have suggested that a change in the fuel chemistry, specifically the change in the number of double bonds in the biodiesel fuel, could be the reason for the increase in NOx emissions, via the prompt NO mechanism [110]. The data shown in this research would support the theory that a reduction in the number of double bounds produces a reduction in the NOx emissions, as shown in Figure 4.9 and Table 4.19. When the hydrogenated biodiesel fuel was used, a reduction in NOx emissions over the conventional biodiesel was achieved.

**Fuel Injection Timing**

The advance of injection timing with biodiesel fuel due to the physical property differences between diesel fuel and biodiesel fuel has been proposed and shown to be a
contributor to the NOx emission increase [103]. In this research, the needle lift data from fuel injector #1 was collected for each fuel and for each mode. As shown in Figures 4.25 through 4.28, the needle lift for each fuel had a pilot and a main pulse which did not change timing regardless of fuel. This corresponds with the data previously for this engine and observations regarding common rail engines [121, 201]. The common rail engine seems to be less affected by a change in the fuel composition with regard to fuel injection timing. However, as shown in the needle lift figures, there were some changes in the needle lift for the biodiesel fuels, indicating an increase in pressure to increase the height of the needle, thus allowing more fuel to enter the cylinder in a fixed timing.

**Cetane Number**

Previously, it has been expected that higher cetane number fuels will produce shorter pre-mixed burn fractions and thus lower NOx emissions [42]. In this research, the hydrogenated biodiesel has a higher cetane number and lower NOx emissions, as shown in Table 4.9 and Figure 4.9. While this fits the stated theory, the soy-based biodiesel also has a cetane number higher than diesel fuel and lower than the hydrogenated biodiesel fuel. As shown in the NOx emissions results, Figure 4.9, the soy-based biodiesel produced NOx emissions higher than the diesel, while the hydrogenated biodiesel produced NOx emissions at the same rate as the diesel fuel or lower than the diesel fuel.

**Mixture Stoichiometry at Lift Off Length**

Cheng and coworkers suggest that the mixture stoichiometry at the lift-off length of the fuel from the injector nozzle may be different between diesel and biodiesel and
thus plays a role in the NOx increase, but the mechanisms for this are unknown [42]. In Cheng and coworker’s research, the fuel spray penetration lengths were used to adjust the actual start of injection for each fuel to be able to exactly match the start of combustion by knowing the ignition delay [42]. While some experimental information is provided, it is unclear what changes were made in either the injection timing delay or pressure. However, their research provides insight that the spray, droplet break up, and fuel vaporization at the lift-off length are unknowns. The research in this thesis does not support or refute this theory. Injection pressure was allowed to vary with respect to the injection timing. It is unknown if higher injection pressures produce longer lift-off lengths.

**Oxygen Content of the Fuel**

Some researchers suggest that the higher oxygen availability in the combustion chamber as a result of the oxygen in the fuel contributes to the NO formation process [126, 127]. This research compared two different biodiesel fuels with similar blend concentrations in diesel fuel. After calculating the oxygen content by methyl ester carbon chain lengths, it was found that the oxygen content of the fuels is similar, as shown in Table 4.19. Table 4.20 shows the ratios between carbon, hydrogen and oxygen for the two fuels. The carbon to oxygen ratio is essentially the same for each fuel. While the oxygen concentrations are similar, the NOx reductions are not, and thus no correlation can be made. Therefore, the fuel bound oxygen would not be attributed to be a contributing factor in the NOx effect.
Fuel Spray Characteristics

The fuel spray characteristics, including droplet size distribution, droplet inertia, air entrainment, penetration in cylinder, evaporation rate, and heat dissipation are affected by the various fuel properties [95]. These fuel properties include viscosity, surface tension, cetane number, and the boiling range temperature of the fuels [95].

In a recent article by Boulanger and coworkers, the liquid properties of the C18 methyl ester were compared to a C12 alkane representing diesel fuel to gain some insight into the change in physical properties of the fuel and how they affect NOx emissions [204]. For this simulation, C12 and C7 alkanes were chosen to serve as the reference case (n-dodecane for the liquid properties and n-heptane for the gaseous phase combustion properties). The model compound to represent biodiesel was methyl linoleate. The differences in the fuel properties and behavior were divided into 4 groupings: 1) vapor pressure, heat of vaporization, and surface tension; 2) thermal conductivity within the droplet and heat capacity of the liquid; 3) density and viscosity changes, split into two sub-groups to separate the effect of dynamic viscosity from density; 4) full set of biodiesel properties [204]. Some interesting points from their findings:

<table>
<thead>
<tr>
<th>Ratio</th>
<th>B100</th>
<th>H100</th>
</tr>
</thead>
<tbody>
<tr>
<td>H/C</td>
<td>1.81287</td>
<td>1.87809</td>
</tr>
<tr>
<td>C/H</td>
<td>0.55161</td>
<td>0.53246</td>
</tr>
<tr>
<td>C/O</td>
<td>9.17032</td>
<td>8.88758</td>
</tr>
</tbody>
</table>
- It is expected that combustion takes longer for biodiesel and needs more time to vaporize as a result of the higher volatility, higher viscosity, and surface tension. The higher viscosity and surface tension diminish the break-up efficiency if the fuel, thus favoring the diffusion mode of combustion.

- Weaker fuel spray break-up due to higher viscosity of the fuel alone with no change in spray density advances the onset of heat release. Their data suggests this, but they could not give an explanation for it.

- Slower vaporization produces higher temperatures that last longer in the combustion cycle.

- It was believed that momentum due to larger density helped to maintain droplet velocity and break-up in the long term.

- A larger kinematic viscosity tends to lead to larger droplet size (Sauter mean diameter).

- Because of slower evaporation, peak temperature occurs later during the expansion stroke and tends to be lower, but is higher during the end of the cycle.

- The pressure traces of their research show that combustion phasing is governed by physical properties.

- They conclude from their work that biodiesel NOx is a result of lower vaporization rate causing a longer spray penetration, the evaporating droplets sweeping a larger volume which cause fuel release into a larger ignitable zone, due directly to the lower volatility of the fuel. The
volume of the reaction zone increases with higher temperatures. This wider ignitable zone is suspected to contribute to the NOx increase.

- When the kinematic viscosity and density of the fuel increase, the high temperature zone volume is not well developed and thus the maximum temperature is lower.

As is seen from the fuel property data for this research, section 4.7, the B100 and the H100 have higher kinematic viscosities than diesel fuel. Thus, the advance in the start of combustion for the B100 and higher NOx could be attributed to the increased kinematic viscosity. However, the in-cylinder data does not show any effect of advance in start of combustion with the biodiesel fuels. From a analysis of the density of the fuels used, the densities of both the B100 and H100 are comparable, and slightly higher than the diesel fuel (BP15 .8339 g/ml; B100 .87785 g/ml; H100 .87276 g/ml). Volatility information for the fuels is not available for comparison. Therefore, it is unclear if Boulanger and coworkers theory that the higher density and lower volatility both produce a longer vaporization and larger droplets spray field zone, thus causing higher NOx emissions, would provide a good explanation for the emissions seen in this research.

**4.8.2 Fuel Injection Strategy on NOx emissions**

Several researchers have studied the effect of the multiple pulse injection and its impact on the combustion characteristics and emissions from diesel engines both with diesel and biodiesel fuels [122, 123, 200, 205]. The following section discusses their findings and relates them to the current body of research.
Choi and coworkers tested the effect of biodiesel fuels blends and multiple injections in a diesel engine [122]. In their high load condition, they showed that the NOx emissions between the base diesel and multiple pulse diesel fuel were roughly the same over various start of injection timings. However, when comparing the B20 and B40 blends with multiple injection of biodiesel to diesel fuel, the B20 blend produced more NOx emissions regardless of injection timing, where the B40 blend produced the same or less NOx emissions than diesel fuel. At the low load condition, the double injection with the diesel fuel produced less NOx emissions as the start of injection timing was retarded, producing lower NOx at -1CA ATDC [122]. The impact of the injection timing was also seen in the biodiesel data. As the injection timing was retarded, the multiple pulse biodiesel blends produced less NOx than the single injection of the diesel and biodiesel blends, and less than the double injection of the diesel [122]. The effect of multiple fuel injections on fuel consumption was more significant in the high load than the low load, with increase seen as a function of start of injection timing [122].

Zhang’s work showed how the interval of the pilot from the main fuel pulse could lower the emissions at his low load condition (1600 rpm /58.9 ft-lb) even further than with a single injection without the use of EGR [123]. While smoke emissions are impacted without the use of EGR, the NOx emissions can be managed well without an EGR if a pilot injection is used [123]. He also showed how the size, or the amount of fuel in the pilot, made an impact on NOx emissions.

Tennison and workers showed multiple injections and injection pressure affected the smoke and NOx from an engine [206]. At the same injection pressure, a single injection had a better impact on NOx than a double injection, while smoke emissions
were significantly reduced [206]. In a second study on the pilot timing, as the pilot time was retarded, the NOx decreased and the soot increases. However, as the pilot was advanced closer to the main injection, the NOx increased and the soot decreased [206]. This study definitely showed how low NOx emissions can go with an increase in injection pressure [206]. They also concluded that ignition delay of the pilot quantity was dependent on a chemical delay and not a physical mixing delay, based on the data that showed that the point of ignition for the pilot injection was at the same crank angle regardless of the pilot timing [206].

Carlucci and coworkers studied the effect of the pilot injection on the main fuel injection and then added a third injection called an “early” injection before the pilot injection [205]. With this strategy, they were able to successfully reduce smoke and NOx emissions over various engine conditions [205]. The early pilot strategy of injection of a quantity of fuel very advanced with respect to top dead center allows for the formation of a locally lean mixture in the engine cylinder. This fuel is ignited by the pilot injection. By coupling the two injections, there was a weak heat release produced. An increase in this early duration leads to a main combustion event that has a lower ignition delay and a premixed peak [205]. The experimental results showed that a short early injection coupled with the pilot injection was effective in reducing fuel consumption, NOx and soot levels [205].

As evidenced by the needle lift traces, the injection strategy of the engine for this research involved a pilot and main injection. With that strategy, two distinct heat release peaks were shown in the heat release plot for all 4 engine modes. As indicated by Carlucci’s literature review, the pilot ignition combustion causes a reduction in the
ignition delay of the main injection, and as a consequence, a decrease in the rising rate of the cylinder pressure during the main combustion [205]. As he described it, the pilot injection decreases the ignition delay of the main injection thus reducing the fuel fraction burned during the premixed phase, leading to a reduction in the combustion temperature peak [205]. However, in this research comparing the diesel fuel with the biodiesel fuel blends, there is an observation of NOx emissions reduction with the hydrogenated biodiesel fuel, while there is a NOx increase with the soy-based biodiesel fuel in comparison with the diesel fuel. This would lead one to conclude that while the pilot injection is playing a role in reducing the ignition of the main injection, there is not a consistent NOx emission given for each of the fuels. Thus, there are fuel chemistry differences that must also be playing a role in the changes seen in the NOx emissions.

It should be mentioned that there has been some research with a hydrogenated-like biodiesel. Knothe and coworkers tested a technical grade methyl oleate in a 2003 DDC series 60 diesel engine with direct injection and electronic control [105]. The engine was fitted with high pressure electronic unit injectors, with EGR and an EGR cooler. In their CFR 40 Part 86 Subpart N testing, they showed a 6% increase in the NOx emissions when methyl oleate was used while the biodiesel fuel used showed a 12% increase over diesel emissions [105]. It is unclear from their paper if there was any kind of unique fuel injection strategy during the engine operation. A more recent set of experiments was performed by Tat and coworkers with a biodiesel made form high-oleic soybeans [207]. In their testing, a John Deere 4045T 4.5L 4 cylinder turbocharged direct injection diesel engine was used. In their work, they showed a decrease in NOx emissions as compared to the soy-based biodiesel, but still an increase in NOx compared
with the diesel fuel [207]. The data in their paper indicate that this engine has a single injection pulse, and that the two biodiesel fuels were operating with a start of injection slightly retarded as a result of the isentropic bulk modulus change of the fuels [207]. It is suggested that these two groups of researchers found an increase in the NOx emissions for the high oleic biodiesel in an engine with a single injection pulse. However, what is not clear is the impact of the EGR on the combustion process and on the results of the research.

To clarify the fuel injection strategy question on NOx emissions, an additional test was performed in the DDC 2.5L engine at 1800 rpm and 61 ft lbs torque, at a fixed single injection timing of 7° BTDC. Figure 4.34 shows the NOx data from the single injection case based on the fuel used. The figure shows an increase with the B20 blend over the ULSD, and a decrease with the H20 blend.
On a power basis, the NOx emissions for each biodiesel fuel are observed to be lower than the ULSD diesel fuel, as shown in Figure 4.35. However, the small changes for the B20 are within the error bars for the data points, so nothing definitive can be stated about the difference. The difference between the H20 and the ULSD are significant based on the error bars.

Figure 4.34: NOx (g/kg fuel) for DDC 2.5L engine, 1800 rpm and 61 ft-lb with single injection timing of 7° BTDC, without EGR, comparing ULSD (BP15) to 20% soy-based biodiesel to 20% hydrogenated soy-based biodiesel
Based on the previous two figures, it could be concluded that the fuel injection strategy plays no role in the change in NOx emissions between the fuels. Testing with the neat fuels may increase the differences seen in the emissions, and thus show a clearer trend.

Pressure data is shown in Figure 4.36. The data has a 0.1 crank angle resolution. The pressure traces are similar for each fuel.
Heat Release data is shown in Figure 4.37. As is shown, the heat release for the BP 15 diesel is the highest. The peak duration lasts for an additional crank angle degree over the H20 peak duration. B20 is slightly higher than H20, but follows the same trend in duration as the BP 15 diesel.
Bulk Cylinder Temperature data is shown in Figure 4.38. The temperatures calculated are similar for each fuel.

Figure 4.37: Heat Release (J/deg) for DDC 2.5L engine, 1800 rpm and 61 ft-lb with single injection timing of 7° BTDC, without EGR, comparing ULSD (BP15) to 20% soy-based biodiesel to 20% hydrogenated soy-based biodiesel
Figure 4.38: Bulk Cylinder Temperature (K) for DDC 2.5L engine, 1800 rpm and 61 ft-lb with single injection timing of 7° BTDC, without EGR, comparing ULSD (BP15) to 20% soy-based biodiesel to 20% hydrogenated soy-based biodiesel

Needle Lift data from the instrumented fuel injector is shown in Figure 4.39.

Because the needle lift sensor does not reset to the same location with each injection, the zero axis is normalized for each needle lift trace. As is seen in the figure, the fuel injection starts at -7° BTDC. The B20 and H20 needled lift traces rise faster than the BP
15 diesel, indicating a higher pressure on the needle to deliver the appropriate quantity of fuel to meet the same power requirement. More fuel would be required for the B20 and H20 blends as the energy density of the biodiesel is less than that of the BP 15 diesel fuel.

Figure 4.39: Needle Lift (mm) for DDC 2.5L engine, 1800 rpm and 61 ft-lb with single injection timing of 7° BTDC, without EGR, comparing ULSD (BP15) to 20% soy-based biodiesel to 20% hydrogenated soy-based biodiesel
Based on the combustion data plots presented, the slightly higher and longer
duration heat release for the BP 15 diesel fuel could explain the higher NOx emissions.
However, the needle lift trace shows a shorter (1° in comparison to the B20 and 2° in
comparison to the H20) duration of fueling, which indicates a longer duration of fuel
spray. With a longer duration of fuel spray, there would be a shorter time for NO
emissions, thus a lower amount of NOx. On a fuel basis, the B20 NOx emissions were
higher than the BP 15 diesel fuel. Thus, this increase cannot be explained by the needle
lift data.

4.9 Conclusions

A study was performed to test the effect of NOx reduction from a compression
ignition engine by reducing the iodine value of a biodiesel fuel by hydrogenating it, and
thus changing the fuel properties by increasing the hydrogen content, reducing the double
bonds of the fuel, and increasing its cetane number. The current research presented here
focuses on the emissions from an engine that had the EGR shut off and used a pilot and
main injection strategy. Engine tests were performed to compare this hydrogenated fuel
with a soy-based biodiesel fuel. Two blend concentrations were prepared: a 20% blend
and a 40% blend. The fuels were tested in 4 engine modes, and compared to an ultra low
sulfur diesel fuel. The 20% soy-based biodiesel showed increases in NOx emissions
across the 4 engine modes. The 40% soy-based biodiesel and both hydrogenated
biodiesel blends showed NOx reductions for all 4 engine modes, and in all cases below
the emissions levels for the ultra low sulfur diesel fuel.
From the review of the theories for the NOx increase associated with biodiesel, the following can be said about the data:

- If a higher adiabatic flame temperature indicates an increase in the NOx emissions as a result of the number of double bonds in the biodiesel fuel, then a decrease in those double bounds would lead to a decrease in the NOx emissions. This data and the adiabatic flame temperature calculation support this conclusion.

- Fuel injection pressure increased as the needle lifted higher to deliver the required fuel in the same timing. This increase in pressure and its affect on the NOx emission is unknown.

- It may also be possible that the chemistry of the fuel affects the physical properties of the fuel as it is delivered into the cylinder. Specifically, that the higher density and lower volatility both produce a longer vaporization and a larger droplet spray field zone, thus causing higher NOx emissions. However, the density of the B100 and H100 are similar, which does not explain the reduction in NOx result for the H20 and H40 fuel blends. The boiling range information for the neat fuels shows that the volatility of the biodiesel fuels are similar, and with higher volatility than the BP 15 diesel fuel. Thus, the higher volatility and shorter vaporization would lead to lower NOx emissions. Heat Release data showed similar vaporization, and yet lower NOx emissions with the H20 fuel.
Based on the discussion regarding the theories for the biodiesel NOx effect, the results seen in the NOx emission data would have to be explained by the increase in adiabatic flame temperature for the soy-based biodiesel and the Prompt NOx effect as a result of the change in the biodiesel fuel properties between the soy-based biodiesel and the hydrogenated biodiesel.
Chapter 5

NOx Reduction through Mixed Mode Combustion

5.1 Preface

This chapter presents new data that has not been previously published. Initial research was performed by the author on a Navistar 7.3L heavy duty turbocharged diesel engine. The data from the initial study is presented here. Because the engine’s fuel injection system (Caterpillar’s HEUI fuel injectors- hydraulic electronic unit injectors) produced a multiple pulse (split-shot) injection at the low engine speed and load condition, it was unclear in the heat release data when the dimethyl ether (DME) ignition was occurring and when the diesel fuel ignition was occurring. However, the emissions data from the initial study did suggest a NOx reduction benefit from the DME in a mixed mode combustion system. A second study was then performed in an engine which had fuel injection control and where the impact of the fuel injection timing on the combustion process could be studied more easily during mixed mode combustion. A Detroit Diesel Corporation (DDC) 2.5L light duty turbocharged diesel engine was used in this second study. The engine intake air system was modified to incorporate an air heating system so that the impact of intake air heating on the low temperature heat release ignition could be probed.
5.2 Introduction

Rising fuel prices and government regulated reductions of exhaust emissions continue to pressure engine and vehicle manufacturers to make improvements in efficiency and emissions. Those improvements can be made through changing the fuel, modifying how energy is stored and used on a vehicle, and through improvements in the engine combustion process.

This research plan addresses the issue of reducing emissions while maintaining or improving diesel-like fuel efficiency through a homogeneous fumigated fueling scheme in a turbo diesel engine. In this work, the theoretical concepts of combustion efficiency and emissions of a homogeneous fumigated charge compression ignition process (HCCI) initiated by a pilot fuel injection, or what may be better described as a mixed mode combustion scheme, will be explored.

Dimethyl ether (DME) is a gaseous material used commonly as a propellant in aerosol cans. Also, it has been found to be an effective fuel for use in compression ignition engines due to its high cetane number and smokeless combustion [208]. DME is seen to be an important fuel for worldwide use due to its flexibility for use in home heating, engines, and stationary power, as well as its various potential feedstocks: coal, biomass and natural gas [209]. With the increase in the cost of a barrel of oil, the financial prospects for DME have improved sufficiently to make it a more viable fuel for US interests. Researchers in other countries have been studying the use of DME in HCCI engines [210, 211]. However, the control of ignition timing and combustion duration over a wide range of engine speeds and loads remains a hindrance to the use of HCCI [211].
Therefore, understanding what may affect the ignition and combustion process in an HCCI engine and how it affects the process is a significant need in harnessing HCCI for practical use.

The theme of this research was to explore if a mixed mode combustion system with DME as the gaseous fuel could reduce NOx emissions from a compression ignition engine. A set of initial experiments with DME inducted into the intake of an engine and coupled with a diesel fuel pilot injection were performed. These initial experiments showed that NOx emissions could be reduced with this “mixed-mode” combustion strategy. Engine hardware did not allow for all aspects of the pilot fuel injection timing to be explored, and competing effects of multiple injections skewed some data. The experiments did not completely address how low the NOx emission could go, or how to achieve minimal NOx emissions.

The hypothesis being tested is that through the improvement of the ignition quality of a mixed mode DME/diesel pilot injection compression ignition engine, control of the homogeneous ignition process at the low speed and low load conditions will simultaneously yield lower NOx emissions and similar or improved efficiency. Using the high ignition quality of DME via its low ignition temperature reactions, control of the homogeneous ignition process can be achieved by controlling the reaction rate of the fuel and air mixture.

The reaction rate of the cylinder charge is a function of several variables including intake air temperature, heat addition through compression of the cylinder charge, heat addition through introduction of exhaust gases in the intake charge, cetane number of the pilot fuel injection, cetane number of fuel and gases in the intake air, and
the air/fuel ratio in the cylinder charge. The homogeneous charge fuel for these experiments will consist of DME and mixtures of DME with Methane to study the effect of changes in the cetane number of the cylinder charge. The pilot fuel injections will consist of an ultra low sulfur diesel fuel. An intake air heater will be used to vary the charge temperature as a way to model the impact of adjusting compressive heating and intake air heating effect on the autoignition of the charge.

The research work that will be discussed included several aspects. Those include:

1. Design and test the fueling system on the Navistar 7.3L and the DDC 2.5L engines to introduce the homogeneous mixture into the engine intake port. Show that the engine can be operated at a steady state condition.

2. Perform a series of tests with the Navistar 7.3L to study the effects of varying the concentrations of DME and air in the intake charge. Perform another set of tests with the DDC 2.5L engine to study the effect of varying timing of the pilot injection of the diesel fuel by varying 1) the cetane number of the intake charge with DME and blends of DME and Methane, and 2) the intake temperature of the charge.

3. Explain the behavior of the system through various methods which include:
   - Use the AVL CEB (Combustion Emissions Bench) II to measure the emissions of the process and compare to normal mode operation. With this equipment, changes in NOx, CO, CO₂, Methane and hydrocarbon emissions will be measured. Use a Nicolet FTIR spectrometer to collect exhaust to confirm the N₂O emissions. Use gas chromatography to collect information on the amount of DME and other C1-C6 carbon compounds found in the
exhaust gases. Collect particulate matter emissions to confirm the magnitude of reduction from this mixed mode system.

- Use the pressure trace analysis software to analyze the bulk fuel burning and heat release of the mixed mode process. The data will provide information on the ignition quality of the fuel and the burning rate.

### 5.3 DME and Mixed Mode Combustion Process

The proposed research involves a direct injection diesel engine, operating through the use of DME (dimethyl ether) and Methane blends fumigated in the intake air and ignited through the use of the diesel fuel pilot injection. Therefore, literature relevant to this subject would include any dual fuel concept using DME and diesel pilot injection, in addition to a combination of DME and other gases fumigated in the intake air. DME fuel property information is shown in Table 5.1 [212]. DME has a high cetane number, making it an excellent compression ignition engine fuel [76, 83].
Hountalas and Papagiannakis developed a simulation model for a direct injection, dual fuel, diesel- natural gas engine [213]. Their data was compared to experimental data for diesel fuel only, and showed that the NOx emissions for any of the diesel-natural gas blends was higher than for diesel over the BMEP (brake mean effective pressure) range [213]. Also, the data showed that the PM emissions could be reduced below that for diesel only, with increasing natural gas blends over 30% for the entire BMEP range [213].

Chen and coworkers performed experiments with DME and natural gas blends fumigated into a single cylinder Yanmar engine [214]. Through the significant combustion analysis performed, they showed the effect of increasing DME content in the blend on NOx, thermal efficiency and total hydrocarbons [214]. Their research did not focus on the effect on soot emissions [214]. The data was presented so that one could understand the relationship between the DME concentration, natural gas concentration and the various emissions [214]. Conditions with the highest BMEP and brake thermal

<table>
<thead>
<tr>
<th>Property</th>
<th>DME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>CH₃OCH₃</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>46</td>
</tr>
<tr>
<td>Oxygen content—mass %</td>
<td>34.8</td>
</tr>
<tr>
<td>Stoichiometric air fuel ratio—kg/kg</td>
<td>9.1</td>
</tr>
<tr>
<td>Lower heating value—kJ/kg</td>
<td>28,800</td>
</tr>
<tr>
<td>Liquid density—g/ml@15°C</td>
<td>0.668</td>
</tr>
<tr>
<td>Boiling point—°C</td>
<td>24.9</td>
</tr>
<tr>
<td>Viscosity—kg/m-s@25°C kg/m-s</td>
<td>est. 0.12–0.15</td>
</tr>
<tr>
<td>Vapor pressure@25°C–bar</td>
<td>5.1</td>
</tr>
<tr>
<td>Critical pressure–atm</td>
<td>52</td>
</tr>
<tr>
<td>Critical temperature–°C</td>
<td>127</td>
</tr>
<tr>
<td>Ignition temperature–°C</td>
<td>235</td>
</tr>
</tbody>
</table>
efficiency were also the conditions with the highest total hydrocarbons and NOx emissions [214].

The HCCI combustion process has more premixed heat release than the typical diesel combustion process, sometimes with a two stage heat release depending on the fuel used [215]. Therefore, the injection timing, fuel vaporization, and ignition timing are critical to occur in sequence to produce maximum engine power output, usually at top dead center (TDC). The ignition timing is specifically a function of the chain initiation and chain propagation reactions which begin the autoignition process, and are controlled through the heating of the fuel and air mixture. To that end, the ignition timing is a function of the fuel blend and in-cylinder conditions. When a gaseous fuel is used in the engine, the fuel vaporization process does not exist. Additionally, the mixture preparation of the fuel and air mixture is an important quality affecting the homogeneity of the combustion. Research has shown that HCCI can be effective to reduce emissions and improve efficiency within certain boundaries, broadly the ignition limit and the knocking limit of the fuel blend [214]. The goal of this research is to determine if the ignition quality of dimethyl ether (DME) or blends of DME fumigated into the engine, and then ignited by a diesel fuel pilot injection can produce the desired NOx emissions reduction. Specifically, can the use of a diesel pilot injection of fuel to ignite a homogeneous mixture of DME and air and mixture of DME, Methane and air reduce NOx emissions and particulate matter, while minimizing the typical hydrocarbon and CO increase associated with HCCI combustion? Researchers have used DME blends with other fuels to accelerate the low temperature reactions in the HCCI process, like propane and butane [216, 217]. Some experimental and modeling work with DME and Methane
or natural gas blends has also been performed [218, 219]. However, DME’s use with
Methane and a pilot injection of diesel fuel has not been demonstrated before.

The theoretical concepts of this research center around the low temperature
reactions, the heat release rate, the ignition delay of the bulk fuel, and the NOx
mechanisms. Low temperature reactions are defined as reactions which occur below 600
K [220]. Martinez-Frias and coworkers have shown that the fraction of heat release from
these reactions can be affected by thermally conditioning the intake charge within a 40 K
window of the charge temperature at the beginning of the compression stroke (the
temperature at BDC) [144]. These results were for an engine running at a specific
compression ratio, speed, equivalence ratio, EGR and inlet pressure of air and fuel [144].
Therefore, it is difficult to give an exact temperature range for a specific engine, because
it is a function of the compression ratio of the engine and other heat contributions to the
fuel and air mixture. Heat release rate is defined as the amount of heat released by the
chemically reacting system over time. Controlling the heat release rate is critical to
managing the emissions and peak power output. Ignition delay of the bulk fuel is defined
as the amount of time that it takes for the fuel to begin combustion measured from the
start of injection of the fuel. Researchers define the start of injection as when the fuel
first leaves the nozzle [221]. However, ignition delay means something different when
talking about a gaseous fuel, especially when bringing it into the cylinder through the
intake air system. Since intake air temperature, turbocharging and compression all add to
the energy involved in the ignition process, a new definition of ignition delay may need
to evolve as a part of this research. Some researchers suggest tracking the timing of mass
fraction burned 50% (MFB50) as a means to denote an endpoint to ignition [148, 222, 223].

NOx producing mechanisms include the Zeldovich (thermal) NO, Fenimore (prompt) NO, nitrous oxide (N₂O) generated NO, and conversion of fuel nitrogen to NO [48]. Diesel combustion generates NOx mostly from the Zeldovich mechanism, and some from the Fenimore mechanism due to CH formed in the flame front. However, NO is not typically generated due to fuel nitrogen conversion (as there is none) nor the nitrous oxide (N₂O) pathway. However, researchers are beginning to find that nitrous oxide (N₂O) is being emitted from HCCI engines, suggesting that its abundance shows this pathway is being used to create NO at the lower temperatures [224].

5.4 Design and Testing of the DME Gaseous Fueling System

The first part of the research involved demonstrating that a reduction in NOx emissions could be produced through the induction of DME into the engine. This phase included developing the fuel system to handle DME induction. Hardware was added to the engine intake air system and upstream from the engine intake to provide mixing length for the fuel and air prior to entry into the cylinder via the intake air port. The DME fuel was dispersed and mixed with the boosted air using a custom built mixing manifold. A picture of the fuel aspiration manifold is shown in Figure 5.1. The manifold consisted of four Enerac Hastelloy filters placed on the radial of the manifold.
The DME tank was fitted with tank heaters as shown in Figure 5.2, and pressure and temperature monitoring were added to the DME tank to maintain a constant pressure and temperature of the fuel delivery, as shown in Figure 5.3.
Figure 5.2: DME fuel tank with heaters
Also, this stage included determining how much energy and therefore how much fuel would be required for a specific speed and load (mode) condition based on the mass air flow for that mode running on diesel. The Navistar 7.3L engine was set up to continue to inject the small pilot amount of diesel fuel that would be needed for idling the engine. The approach was to bring in a mixture of fuel and air on the intake stroke, metering the fuel with a Matheson flow meter. Depending on the flow rate required for the particular test, a different Matheson flow tube number was used. This mixture was compressed and would not ignite as it would in a typical HCCI combustion process. The only additional in-cylinder event occurring was the additional diesel fuel pilot and the associated diffusion burning. To prevent purely homogeneous ignition of the intake charge, the fuel and air mixtures in the intake charge were to be leaner than normal HCCI
mixtures. The combustion events were measured using a pressure transducer, and the heat release was determined through the use of a simple heat release equation assuming a constant gamma of 1.37 [11]. For further simplification, heat losses through the cylinder wall were ignored. Monitoring the combustion events via the pressure trace indicated when the knocking limit was reached at a particular speed and load condition.

5.5 Test Results from a Navistar 7.3L Heavy Duty Turbocharged Diesel Engine

A series of tests were conducted on a Navistar 7.3L turbocharged direct injection diesel engine with a modified fueling system permitting a homogeneous charge of DME fuel to be inducted into the intake air system. The fuel was introduced into the intake air system after the charge air cooler, but several feet prior to entering the intake air manifold to allow for mixing of the fuel and air. The test matrix comprised 2 speed and 4 load conditions comparing a normally operating diesel engine fueled by Ultra Low Sulfur Diesel (ULSD) (15ppm sulfur) with a mixed mode combustion engine operating with the same ULSD fuel and the inducted DME, as described in Table 5.2. Also, a series of tests were conducted at a set speed and load condition with varying concentrations of DME, as described below in Table 5.2. These speed and load conditions were picked because they represent the range between 2 and 3.5 bar IMEP (Indicated Mean Effective Pressure) where researchers have had the most success in achieving HCCI combustion [145]. IMEP is defined as the net work generated in the combustion chamber [225]. The DME was increased to a point where the amount of energy input would be equal to the amount of energy supplied by the directly injected diesel fuel.
Table 5.2: Description of Initial Engine Test Plan (ULSD= Ultra Low Sulfur Diesel; DME= Dimethyl Ether)

<table>
<thead>
<tr>
<th>Engine Speed (rpm)</th>
<th>Engine Load (ft-lb)</th>
<th>Engine Combustion Mode</th>
<th>Fuel Type</th>
<th>DME Content (Flow meter scale)</th>
<th>DME Content (gm/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>876</td>
<td>84</td>
<td>Diesel</td>
<td>ULSD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>876</td>
<td>100</td>
<td>Diesel</td>
<td>ULSD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>876</td>
<td>125</td>
<td>Diesel</td>
<td>ULSD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>876</td>
<td>150</td>
<td>Diesel</td>
<td>ULSD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>876</td>
<td>84</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
<td>.7691</td>
</tr>
<tr>
<td>876</td>
<td>100</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
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<td>876</td>
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<td>ULSD &amp; DME</td>
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<tr>
<td>876</td>
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<td>ULSD &amp; DME</td>
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<td>1000</td>
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<td>125</td>
<td>Diesel</td>
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<td></td>
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<tr>
<td>1000</td>
<td>150</td>
<td>Diesel</td>
<td>ULSD</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>1000</td>
<td>84</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
<td>.7691</td>
</tr>
<tr>
<td>1000</td>
<td>100</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
<td>.7691</td>
</tr>
<tr>
<td>1000</td>
<td>125</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
<td>.7691</td>
</tr>
<tr>
<td>1000</td>
<td>150</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>50mm</td>
<td>.7691</td>
</tr>
<tr>
<td>876</td>
<td>84</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>60mm</td>
<td>.9456</td>
</tr>
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<td>876</td>
<td>84</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>70mm</td>
<td>1.1301</td>
</tr>
<tr>
<td>876</td>
<td>84</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>80mm</td>
<td>1.3228</td>
</tr>
<tr>
<td>1000</td>
<td>150</td>
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<td>ULSD &amp; DME</td>
<td>70mm</td>
<td>1.1301</td>
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<tr>
<td>1000</td>
<td>150</td>
<td>Mixed Mode</td>
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<tr>
<td>1000</td>
<td>150</td>
<td>Mixed Mode</td>
<td>ULSD &amp; DME</td>
<td>90mm</td>
<td>1.5237</td>
</tr>
</tbody>
</table>

ULSD- Ultra Low Sulfur Diesel (15ppm)

Since the goal of this research is to reduce NOx emissions and to improve fuel efficiency, gaseous emissions data and combustion pressure traces were collected.

Figure 5.4 shows that through the induction of DME in the intake, NOx emissions were reduced for both speed conditions versus the baseline, and were reduced as the load was increased in each speed condition. On further inspection, there was a significant decrease in the NO emission, shown in Figure 5.6, while the NO2 emissions increased, as seen in
Figure 5.5. Although not shown in this report, there was a significant increase in both CO and HC (hydrocarbon) emissions.

Figure 5.4: NOx emissions in gram NOx per kg fuel (Test Condition = Speed (rpm)/Load (ft-lbs)) ; Baseline is ULSD diesel fuel.
Figure 5.5: NO emissions (gram NO/hour) (Test Condition = Speed (rpm)/Load (ft-lbs)) ; Baseline is ULSD diesel fuel.
Figure 5.7 is a graph of the brake specific energy consumption. As can be seen, the engine was operating at a higher fuel/energy consumption rate (BSEC) over most test conditions. Although the goal of the test was to keep the speed, load and fuel energy content the same, this was not possible due to the engine control module (ECM). It seems that as the DME content was increased into the engine, the ECM began to dial back on the amount of diesel fuel injected as well as to adjust the fuel injection timing and injection pressure, possibly as a function of the fueling map of the engine. This is shown in Table 5.3 for the tests composed of holding speed and load constant and varying the DME concentration in the intake air. However, for all speed and load conditions, constant speed and load were maintained throughout the test.
Figure 5.7: Brake Specific Energy Consumption (MJ/ hp-hr); Baseline is ULSD diesel fuel.
The following figures, Figure 5.8 and Figure 5.9, show a comparison in the heat release for two speed and load conditions, specifically 876 rpm and 84ft-lb torque, and 1000 rpm and 150 ft-lb torque. A baseline diesel heat release curve is plotted to contrast the change in the heat release curves as the DME concentration being inducted is increased. As can be seen in both cases, heat release rate decreases during the combustion process, with increasing heat loss in the chamber to the cylinder gases either before the main heat release or between the primary and secondary heat release. Some heat release curves show the typical two stage heat release as shown in some HCCI studies [220]. The negative temperature regime is to be expected between the cool flame and hot flame heat release [140]. However, in this engine configuration, there are two pulses of fuel delivered at 876 rpm. After studying the fuel injection timing, the likely cause of the significant negative heat release is the diesel fuel vaporization.

Table 5.3: Breakdown of fueling and injection conditions (Negative Dynamic Injection Timing indicates before TDC)

<table>
<thead>
<tr>
<th>Speed (rpm)</th>
<th>Torque (ft-lbs)</th>
<th>Fuel-Diesel (g/s)</th>
<th>Fuel-Diesel (g/rev)</th>
<th>DME Flow (g/s)</th>
<th>DME Flow (g/rev)</th>
<th>Total Fuel Flow (g/s)</th>
<th>Vol Fuel Desired (Diesel)</th>
<th>Dynamic Injection Timing (Diesel)</th>
<th>Injection Control Pressure (Diesel)</th>
</tr>
</thead>
<tbody>
<tr>
<td>873.8</td>
<td>84.380</td>
<td>0.7532</td>
<td>0.0517</td>
<td>0.0000</td>
<td>0.0000</td>
<td>0.7815</td>
<td>15.5500</td>
<td>-7.6461</td>
<td>3.5004</td>
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<tr>
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<td>0.4739</td>
<td>0.0326</td>
<td>0.7691</td>
<td>0.0528</td>
<td>1.2434</td>
<td>9.9750</td>
<td>-7.6727</td>
<td>3.5066</td>
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<td>0.6253</td>
<td>0.0429</td>
<td>0.9456</td>
<td>0.0649</td>
<td>1.5777</td>
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<td>0.0204</td>
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<td>0.0776</td>
<td>1.4466</td>
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Figure 5.8: Heat Release data for 876 rpm and 84 ft-lb torque with increasing DME concentration in comparison to the baseline diesel operation.
The graphs suggest to further inspect the combustion flame temperatures and pressure traces for each test condition from the current data set, and to continue with further testing to separate the fuel pulse vs. the DME fueling. Chemkin analysis can aid in the explanation of the heat release rate, kinetics of the process, and change in NOx emissions production. Specifically, it is important to know how the mixed mode process is changing the NOx pathway, and if N₂O is produced or acting as an intermediate.

Figure 5.9: Heat Release data for 1000 rpm and 150 ft-lb torque with increasing DME concentration in comparison to the baseline diesel operation.
5.6 DDC 2.5L Light Duty Turbocharged Diesel Engine Tests

This research involves a second set of tests to explore the ignition quality of DME in an engine that will allow for control of injection pulse and timing control. The engine used for these experiments is a Detroit Diesel Corporation 2.5L light duty turbocharged diesel engine. The diesel fuel used is a British Petroleum 15 ppm sulfur ultra low sulfur diesel fuel, listed as BP15 on the figures for the results. When the DME is introduced, it represents the % energy equivalent substitution for the diesel fuel in combination with the rest of the fuel being BP15. For example, BP15 25% DME represents BP15 with 25% energy equivalent DME. The following section gives an overview of the experiments involved in this research.

The second set of experiments involve setting the engine into a single pulse injection mode and spanning DME concentrations to study the effect of the DME on the gaseous and particulate matter emissions for a particular speed and load condition.

For the third set of experiments, thermal conditioning of the intake charge is altered. An intake air heater is installed in the intake air system of the DDC 2.5L engine. The goal of using intake air heating is to observe the effect of this change on the ignition timing and combustion of the charge. Gaseous and particulate matter emissions are collected.

A fourth set of experiments involve modifying the ignition quality of the system by adjusting the cetane number to further reduce NOx emissions and improve efficiency. The fuel brought into the intake is a combination of DME and Methane. Again, there is a pilot injection of diesel fuel. Gaseous and particulate matter emissions are collected.
5.7 Description of Experimental Set-up

The engine tests were performed in a DDC 2.5L engine with a modified intake air system which was designed to allow for intake air heating. The intake air heating will be used to study the ignition behavior of the fuel. Also, the intake air system was modified to host a series of ports for the gaseous fuel blends to be input into the system. Figure 5.10 shows the layout of the intake air heaters before installation of the DDC 2.5L engine. The two Sylvania 20 Watt air heaters were located in parallel with the intake air flow.

Figure 5.10: Layout of intake air heating system before installation on the DDC 2.5L engine stand

The standard fuel injection strategy is comprised of a pre-injection followed by a main injection to reduce emissions and engine noise. For these tests, the engine was
commanded to provide a single pulse injection mode. The experimental tests were performed at: 1800 rpm, 61 ft-lbs torque, and a start of fuel injection timing of 7° BTDC.

5.8 Results from a DDC 2.5L Turbo Diesel Engine

The following sections are the results for the three sets of experiments described previously. Each experiment will be described with the gaseous and particulate matter emissions following.

5.8.1 Increasing Dimethyl Ether Concentrations in Intake Air

The second set of experiments involved setting the engine into a single pulse injection mode and spanning DME concentrations to study the effect of the DME on the NOx emissions for a particular speed and load condition. The concentrations of DME are represented as the percent energy equivalent substitution by DME that replaced the diesel fuel energy, based on the calorific value of the fuels. Gaseous and particulate matter emissions were collected.

Figure 5.11 shows the NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. NOx emissions decrease slightly per gram of fuel, approximately 10%, but there is no decrease observed with increasing DME fumigated fuel.
Figure 5.1.12 shows NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. On the basis of power, a greater impact in NOx emissions reduction is observed than for the conventional diesel BP15.
Figure 5.12: NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air

Figure 5.13 shows the NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. As is seen in the figure, for a DME concentration of 15% energy equivalent, an almost 50% percent reduction in NO emissions is observed. As the DME % is increased, the NO emissions begin to increase.
Figure 5.14 shows the NO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. As is seen in the figure, for a DME concentration of 15% energy equivalent, an almost 50% percent increase in NO₂ emissions is observed. As the DME % is increased, the NO₂ emissions begin to decrease.
The Nicolet Magma 500 FTIR was used to collect N$_2$O data for the 15% DME and 20% DME Mixed Mode Combustion data points. No N$_2$O was observed with these two concentrations, so the collection of this data was discontinued.

Figure 5.14: NO$_2$ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

The Nicolet Magma 500 FTIR was used to collect N$_2$O data for the 15% DME and 20% DME Mixed Mode Combustion data points. No N$_2$O was observed with these two concentrations, so the collection of this data was discontinued.

Figure 5.15 shows the Brake Specific Fuel Consumption (BSFC) (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. Approximately the same amount of fuel mass was required to maintain the engine speed and load.
Figure 5.16 shows the Brake Specific Energy Consumption (BSEC) (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. On an energy basis, as the percent of DME energy was increased, less energy was required to produce the same amount of power. At the 44% DME energy equivalent, 22.8% less energy was required to maintain the same power output from the engine.
Figure 5.16: Brake Specific Energy Consumption (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

Figure 5.17 shows the CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. As is seen in the figure, with any blend concentration of DME, CO increases over the normal diesel fuel. The maximum CO is measured at 25% DME concentration, with CO decreasing from there whether the blend concentration is increased or decreased.
Figure 5.17: CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

Figure 5.18 shows the Total Hydrocarbons (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. The hydrocarbons increase with increasing percent DME concentration.
Figure 5.19 shows the data from the GC that was collected on the FID. The gases that were calibrated on the GC are shown and quantified. As can be seen, with increasing DME concentration, the amount of DME found in the exhaust gases increase. Also, the Methane concentration is seen to increase. THC is the total hydrocarbons of all those measured from the GC found in the exhaust gas. While not easily shown in this figure, but observed in the data is that the small concentrations of light hydrocarbons other than Methane and DME decrease to zero when using the fumigated DME.
Figure 5.19: GC Data: BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC

Figure 5.20 shows the CO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. An approximately 5% reduction of CO₂ is observed for some DME blend concentrations, but the trend is not consistent.
Figure 5.20: CO$_2$ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

Figure 5.21 shows Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. Methane is a maximum at the 25% DME concentration.
Figure 5.21: Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

Figure 5.22 shows Exhaust Temperatures (°C) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. The exhaust temperature is the same for each test condition.
Figure 5.23 shows Cylinder Pressure trace data for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC. The BP15 diesel pressure trace shows the distinction between the premixed and the diffusion burn parts of the process. As the DME concentration is increased, the start of combustion comes earlier and with it is premixed burning. The premixed phase and the diffusion phase merge. In addition, the pressure increases with increasing DME concentration.
Figure 5.23: Cylinder Pressure Traces (bar) for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC.

Figure 5.24 shows heat release rate (J/deg) for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC. DME exhibits a two peak heat release, the first a low temperature heat release (LTHR) and the second a high temperature heat release (HTHR). With increasing DME concentration, the LTHR peak increases and maintains the same combustion phasing.
However, as the DME concentration is increased, the HTHR peak increases and advances closer to the LTHR peak. In addition, the heat release from the diesel fuel is decreased with increasing DME concentration and maintains the same combustion phasing.

Figure 5.24: Heat Release Rate (J/deg) for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC
Figure 5.25 shows bulk cylinder temperature (K) for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC. With increasing DME concentration, the bulk temperature occurs earlier and an overall increase in bulk temperature occurs.

Figure 5.25: Bulk Cylinder Temperature (K) for BP15 in comparison to mixed mode combustion with increasing energy equivalent percent DME concentration at 7° BTDC
The following figures show the results of fixing DME concentration at 25% energy equivalent while changing in injection timing. All results are shown in comparison to diesel fuel (BP15) at 7° BTDC.

Figure 5.26 shows NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timing. As the injection timing is retarded, the NOx emissions decrease. The decrease in the NOx emissions as the injection timing is retarded would be expected since there would be less time for the production of thermal NO until the exhaust valve opens and quenches the reactions.

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![Bar chart showing NOx emissions for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timing.](image)

**Figure 5.26:** NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.
Figure 5.27 shows NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. As the injection timing is retarded, the NOx emissions decrease. For the same power output, NOx emissions were reduced by almost 50% by injection of the diesel fuel at 1° BTDC.

Figure 5.27: NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings

Figure 5.28 shows NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. As the injection timing is retarded, the NO emissions
decrease. For the same power output, NO emissions were reduced by over 80% by injection of the diesel fuel at 1° BTDC.

Figure 5.28: NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings

Figure 5.29 shows NO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. While NO₂ emissions increase with DME concentration, they decrease as the injection timing is retarded.
Figure 5.29: NO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.

Figure 5.30 shows Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. Methane emissions increase when injection timing is retarded.
Figure 5.30: Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.

Figure 5.31 shows GC data for 25% energy equivalent DME concentration at varying pilot injection timing: 7°, 5°, 3° BTDC. As the injection timing is retarded and injection begins later, the Methane concentration in the exhaust increases, while the DME concentration stays roughly the same.
Figure 5.32 shows Brake Specific Fuel Consumption (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. Besides a slight decrease in fuel consumption when using DME, there is no apparent change in fuel consumption with change in injection timing.
Figure 5.33 shows Brake Specific Energy Consumption (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.
Figure 5.33: Brake Specific Energy Consumption (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.

Figure 5.34 shows Fuel Consumption (g/hr) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. At 5° BTDC, a minimum fuel consumption is observed, about a 5% decrease when DME is fumigated. As the injection timing retarded, the fuel consumption increases back to the same level as diesel fuel.
Figure 5.34: Fuel Consumption (g/hr) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.

Figure 5.35 shows Cylinder Pressure (bar) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. As the timing is retarded, the crank angle degree of peak pressure shifts while the magnitude of peak pressure remains the same.
Figure 5.36 shows heat release rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. As the timing is retarded, the crank angle degree phasing of LTHR and HTHR remains the same despite the diesel pilot injection. Thus,
the DME portion is independent of the diesel portion. The timing of the diesel fuel heat release adjusts with the change in injection timing. Also, as the timing is retarded, it appears that the heat release from the diesel fuel portion increases.

Figure 5.36: Heat Release Rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings
Figure 5.37 shows bulk cylinder temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings. As the timing is retarded, the bulk temperature as a result of the LTHR and HTHR peak appears to be same. There is a delay and a reduction in the high temperature peak as a result of the retarding of the injection timing and the diesel fuel impact on the combustion process.
Figure 5.37: Bulk Cylinder Temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various injection timings.
5.8.1.1 Sierra Instruments BG-2 Gravimetric Particulate Matter Data

Exploratory observations were made with the BG-2 on the particulate matter (PM) change associated with the mixed mode combustion process. The following photographs show an observed change in the darkness of the filters. Darkness of the filter is related to particulate mass concentration. Again, the engine speed was 1800 rpm and the load was 61 ft-lbs torque for all data collected in these pictures.

An overview of the PM emissions for BP-15 is shown in Figure 5.38 with changing injection timing. The earlier that the fuel injection occurred, the darker the PM was on the filter.

Figure 5.38: BP-15 1800 rpm 61 ft-lbs: 3°, 5°, 7°, 9° BTDC (left to right)

Figure 5.39 shows BP-15 with 25% energy equivalent DME: 1°, 3°, 7° BTDC (left to right). Based on the darkness only, it appears that the particulate matter mass is the same as the injection timing is advanced.
Figure 5.39: BP-15 with 25% energy equivalent DME: 1°, 3°, 7° BTDC (left to right)

Figure 5.40 shows BP-15 with 40% energy equivalent DME: 2°, 3°, 5°, 7° BTDC (left to right). Based on the darkness only, it appears that the particulate matter mass is the same as the injection timing is advanced. Also, comparing the 25% energy equivalent and the 40% energy equivalent, it appears that the particulate matter is the same regardless of DME energy equivalent.
Figure 5.41 shows BP-15 with 40% energy equivalent DME: 7° BTDC (left) and BP-15 with 50% energy equivalent DME: 7° BTDC (right). Based on the darkness only, it appears that the particulate matter mass is decreasing in darkness as DME energy equivalent is increased from 40% to 50% for the fixed injection timing. As is seen in the 50% energy equivalent DME: 7° BTDC (right), the filter appears to be somewhat gray, which indicates less mass on the filter.
Figure 5.42 shows BP-15 1800 rpm 61 ft-lbs: 3° BTDC (top left), 7° BTDC (bottom left) and BP-15 with 25% energy equivalent DME : 3° BTDC (top right), 7° BTDC (bottom right). Based on the darkness only, it appears that the particulate matter for both BP-15 with 25% energy equivalent DME : 3° BTDC (top right), 7° BTDC (bottom right) are similar in mass, yet with retarded injection timing the filter is not as dark. In comparison, the BP-15 1800 rpm 61 ft-lbs: 3° BTDC (top left), 7° BTDC (bottom left) shows dramatic changes in darkness depending on the injection timing with the change in darkness indicating more particulate matter mass as the injection timing is retarded.
5.8.1.2 Tapered Element Oscillating Microbalance (TEOM) and Scanning Mobility Particle Sizer (SMPS) Data

The following section presents data taken from the TEOM and the SMPS.

Figure 5.43 shows TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air. As is seen in the figure, the mass of PM increases with increasing DME concentration.
Figure 5.43: TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with increasing DME concentration fumigated in the intake air.

Figure 5.44 shows TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various fuel injection timings. As is shown in the figure, the maximum PM emissions appears at 5°BTDC, and declines with advanced and retarded injection timing from this point. BP15 gave the lowest PM per power output from the engine.
Figure 5.44: TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various fuel injection timings.

Figure 5.45 shows SMPS data for BP-15 at 1800 rpm and 61 ft-lbs, comparing the particle size distribution with the Thermal Denuder at 40°C and 350°C. As the temperature is increased, the hydrocarbons are volatilized from the soot. Therefore, a shift in the distribution curve is observed which reflects that roughly 1/3 of the particles have been removed by the thermal denuder. The distributions are monomodal.
Figure 5.45: SMPS Data: BP-15 1800 rpm 61 ft-lbs comparing with the Thermal Denuder at 40°C and 350°C

Figure 5.46 shows SMPS data for BP-15 at 1800 rpm and 61 ft-lbs compared with the particle size distribution with the Thermal Denuder at 40°C and 350°C and for BP-15 with 25% energy equivalent DME addition at 1800 rpm and 61 ft-lbs compared with the particle size distribution with the Thermal Denuder at 40°C and 350°C. Both fuels and thermal denuder conditions show a monomodal distribution. This figure shows a reduction of solid and condensed particle concentrations and a shift toward larger remaining particles for DME. Also, the curves that were collected for the fumigated DME did not completely finish at the zero axis, indicating that more particles at the higher size range exist.
Figure 5.46: SMPS Data: BP-15 1800 rpm 61 ft-lbs comparing with the Thermal Denuder at 40°C and 350°C and SMPS Data: BP-15 with 25% energy equivalent DME 1800 rpm 61 ft-lbs comparing with the Thermal Denuder at 40°C and 350°C.

Figure 5.47 shows SMPS data for BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 7° BTDC and data for BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 3° BTDC. As the injection timing is retarded, a 25% increase of the solid and condensed particle concentrations is observed.
Figure 5.47: SMPS Data: BP-15 with 25% energy equivalent DME 1800 rpm 61 ft-lbs comparing with the Thermal Denuder at 40°C and 350°C at 7° BTDC and SMPS Data: BP-15 with 25% energy equivalent DME 1800 rpm 61 ft-lbs comparing with the Thermal Denuder at 40°C and 350°C at 3° BTDC
5.8.2 Impact of Intake Air Heating

For the third set of experiments, thermal conditioning of the intake charge was altered. An intake air heater was installed in the intake air system of the DDC 2.5L engine. The goal of using intake air heating was to observe the effect of this change on the ignition timing and combustion of the charge. Gasesous and particulate matter emissions were collected.

Figure 5.48 shows NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature increases, the amount of NOx emissions increases for the 25% DME mixed mode combustion. However, at the highest temperature, 80°C, for the 25% DME mixed mode combustion, the amount of NOx emissions is over 10% less than that with BP15 diesel fuel for 70°C.
Figure 5.48: NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.49 shows NOx (g/kWh) for Mixed mode combustion at 1800 rpm and 61 ft-lb Torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. On a power basis, as the intake air temperature increases, the amount of NOx emissions increase for the 25% DME Mixed mode combustion. However, at the highest temperature, the amount of NOx emissions is almost 20% less than that with BP15 diesel fuel.
Figure 5.49: NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.50 shows NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature increases, the amount of NO emissions increase for the 25% DME Mixed mode combustion. However, at the highest temperature, the amount of NO emissions is 50% less than that with BP15 diesel fuel. At the intake air temperature of 70 °C, the amount of NO emissions has been reduced by more than 50% with the 25% DME energy equivalent Mixed mode combustion over the BP15 diesel fuel.
Figure 5.50: NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.51 shows NO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature increases, the amount of NO₂ emissions increase for the 25% DME Mixed mode combustion. However, at the highest temperature, the amount of NO₂ emissions is 4 times more than with BP15 diesel fuel.
Figure 5.52 shows Brake Specific Fuel Consumption (BSFC) (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. At the same power, the grams of fuel required was less for the 25% DME mixed mode combustion than with BP15 diesel fuel alone.
Figure 5.52: Brake Specific Fuel Consumption (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.53 shows Brake Specific Energy Consumption (BSEC) (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. At the same power, the energy of fuel required was less for the 25% DME mixed mode combustion than with BP15 diesel fuel alone.
Figure 5.54 shows CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As shown in the figure, the amount of CO was higher with the 25% DME mixed mode combustion than with BP15 diesel fuel alone. As the intake temperature was increased, the amount of CO decreased. For the BP15 diesel fuel, the CO emissions were only 10% of what the same CO emissions with the 25% DME mixed mode combustion.
Figure 5.54: CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.55 shows CO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature was increased, the CO₂ emissions increased for the 25% DME mixed mode combustion. Because of the intake air heating, the density of the air changes, and thus less mass of air is present in the intake air as it is drawn into the engine. This results in less oxygen and nitrogen available in the combustion process, and thus a greater amount of CO₂ because of the change in the mass flow rate of the reactants.
Figure 5.56 shows Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature increased, the Methane decreased for the 25% DME mixed mode combustion. However, there was still 10ppm of Methane for the 25% DME mixed mode combustion at 70 °C temperature while only 2 pm with the BP15 diesel alone.
Figure 5.57 shows Total Hydrocarbons (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. As the intake air temperature increased, the amount of hydrocarbons decreased.
Figure 5.58 shows Exhaust Temperature (°C) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. The temperatures are showing at the top of each bar on the graph. As the intake air temperature increases, the exhaust temperature increases. However, the exhaust temperature does not increase by the same amount that the intake air temperature was elevated to.
Figure 5.58: Exhaust Temperature (°C) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.59 shows the GC Data for BP15 in comparison to mixed mode combustion with 25% energy equivalent DME concentration at 3° BTDC with increasing temperature. As is seen in the figure, as the temperature increases when using DME, the concentration of Methane and DME begin to decrease, which results in an overall decrease in the total hydrocarbon emissions. The figure shows a comparison to the BP15 with increasing temperature. What is also shown with the BP15 increasing temperature is that the small amounts of ethylene and other gases also decrease with increasing temperature. What is also shown more clearly in this figure is the amount of butane that
is observed when using DME, although small in comparison to the Methane and DME observed.

Figure 5.59: GC Data: BP15 in comparison to mixed mode combustion with 25% energy equivalent DME concentration at 3° BTDC with increasing temperature

Figure 5.60 shows Cylinder Pressure (bar) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. With increasing intake air temperature, the peak pressure for the 25% DME mixed mode combustion increases slightly but maintains the same shape and peak pressure.
Figure 5.60: Cylinder Pressure (bar) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.

Figure 5.61 shows heat release rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. With increasing intake air temperature, the LTHR and the HTHR are...
advanced. The peak of the LTHR decreases and the peak of the HTHR increases with increasing intake air temperature. However, the combustion phasing and shape of the heat release for the BP15 diesel fuel remains constant.

Figure 5.61: Heat Release Rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing.
Figure 5.62 shows bulk cylinder temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing. With increasing intake air temperature the bulk cylinder temperature increases.
Figure 5.62: Bulk Temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated in the intake air at various intake air temperatures compared to BP15, all at 3° BTDC fuel injection timing
Figure 5.63 shows TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated with increasing intake air temperature. As intake air temperature increase for the 25% DME mixed mode combustion, the mass of particulate increases per power output.

Figure 5.63: TEOM data for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% energy equivalent DME concentration fumigated with increasing intake air temperature

Figure 5.64 shows SMPS Data for BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 3° BTDC with an Intake Air Temperature of 25°C and SMPS Data for BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 3° BTDC with Intake Air Temperature at 70°C. This data is also
compared to the BP15 conventional diesel at the same injection timing (red and blue lines in the figure) with an Intake Air Temperature of 25°C. As the intake air temperature increases for the 25% DME mixed mode combustion, the number density of condensed particles in this size range increases, but the number of solid particles remains approximately the same with a shift towards larger particles. Also, as indicated in the curve trends with increase intake air temperature, the peak maximum shifts towards larger particles. In comparison to the BP15 conventional diesel, the 25% DME mixed mode combustion has 2/3 more solid particles.

Figure 5.64: SMPS Data: BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 3° BTDC with an Intake Air Temperature of 25°C and SMPS Data for BP-15 with 25% energy equivalent DME at 1800 rpm and 61 ft-lbs compared with the Thermal Denuder at 40°C and 350°C at 3° BTDC with Intake Air Temperature at 70°C
5.8.3 Impact of Change in Cetane Number of the Fumigated Fuel

A fourth set of experiments involved modifying the ignition quality of the system by adjusting the cetane number of the fumigated fuel to further reduce NOx emissions and improve efficiency. The fuel brought into the intake was a combination of DME and Methane. Again, there was a pilot injection of diesel fuel. Gaseous and particulate matter emissions were collected.

Figure 5.65 shows NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. There was no change in NOx emissions with the addition of Methane in the intake air. NOx emissions were reduced when the injection timing was retarded, but increased with increasing intake air temperature.
Figure 5.65: NOx (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.

Figure 5.66 shows NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without % SLPM Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. With the addition of 25% DME, on a power basis, the NOx emissions were reduced by approximately 10%. When Methane was added to the intake air, another 5% NOx was reduced based on power output. NOx emissions were reduced when the injection timing was retarded, but increased with increasing intake air temperature.
Figure 5.66: NOx (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1° BTDC fuel injection timing.

Figure 5.67 shows NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1° BTDC fuel injection timing. As is shown in the figure, the 25% DME mixed mode combustion achieves a 50% reduction in NO emissions on a fuel basis. However, when including Methane in the fumigation gases, this decrease is reduced to 35%. NO is further reduced by retarding injection timing, but increase with increasing intake air temperature.
Figure 5.67: NO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.

Figure 5.68 shows NO$_2$ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. NO$_2$ emissions increase by 175% over the BP15 diesel fuel with the addition of 25% DME mixed mode combustion, and that is reduced to 125% with the addition of Methane into the fumigated fuels. The NO$_2$ is further reduced when the injection timing is retarded, but there is very little effect on NO$_2$ with increasing intake air temperature.
Figure 5.68: NO\textsubscript{2} (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.

Figure 5.69 shows Brake Specific Fuel Consumption (BSFC) (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. On a power basis, there is less mass of fuel required for the 25% DME mixed mode combustion and with Methane. However, as injection timing is retarded and intake air temperature is increased, no change in fuel consumption is observed.
Figure 5.69: Brake Specific Fuel Consumption (g/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing

Figure 5.70 shows Brake Specific Energy Consumption (BSEC) (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. On a power basis, there is less fuel energy required for the 25% DME mixed mode combustion and with Methane. However, as injection timing is retarded and intake air temperature is increased, no change in fuel consumption is observed.
Figure 5.70: Brake Specific Energy Consumption (MJ/kWh) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.

Figure 5.71 shows CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As seen in the figure, adding the Methane to the fumigated DME reduced the CO emissions. When the injection timing was retarded, the CO emissions were increased. Intake air heating made the biggest impact on CO emissions by reducing it by over 50% from the unheated case.
However, the CO emissions from all of these cases were still 6 to 10 times the amount in comparison to BP15 diesel fuel.

Figure 5.71: CO (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing

Figure 5.72 shows Total Hydrocarbons (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As seen in the figure, adding the Methane to the fumigated DME increased the hydrocarbon emissions. When the injection timing was retarded, the hydrocarbon emissions were increased. Intake air heating made some impact on hydrocarbon emissions, but was still 20% more than the case with 25% DME mixed mode combustion. However, the hydrocarbon
emissions from all of these cases were still 1.5 to 3 times the amount in comparison to BP15 diesel fuel.

Figure 5.72: Total Hydrocarbons (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing

Figure 5.73 shows CO₂ (g/kg fuel) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As seen in the figure, adding the Methane to the fumigated DME increased the CO₂ emissions. When the injection timing was retarded, the CO₂ emissions were decreased. When the intake air was heated, the CO₂ emissions increased. However, the CO₂ emissions from all of these cases were higher in comparison to BP15 diesel fuel. Because of the intake air heating, the density of the air changes, and thus less mass of air is present in the intake air as it is
drawn into the engine. This results in less oxygen and nitrogen available in the combustion process, and thus a greater amount of CO₂ because of the change in the mass flow rate of the reactants.

Figure 5.74 shows Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As shown in the figure, Methane emissions increased in the exhaust gas for all cases but the BP15 diesel fuel
case. While a little Methane was being formed for the 25% DME mixed mode combustion case, for the cases where Methane was being added to the fumigated fuel blend, the highest amounts were found in the exhaust by a factor of 6 to 8 times.

Figure 5.74: Methane (ppm) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing

Figure 5.75 shows Exhaust Temperature (°C) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. Exhaust
temperature is fairly constant for this set of test conditions, except in the cases where the intake air temperature was increased.

Figure 5.75: Exhaust Temperature (°C) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1° BTDC fuel injection timing.

Figure 5.76 shows GC Data for BP15 in comparison to mixed mode combustion with 25% energy equivalent DME concentration and with 25% energy equivalent DME concentration at various injection timing and with increasing temperature. When the engine is operated with DME and with a Methane blend fumigated in the intake, more Methane is observed in the exhaust in comparison to the same DME concentration without the Methane fumigated in the intake air. Retarding the injection timing towards
TDC yields an increase in Methane emissions regardless of the Methane fumigation in the intake air. Increasing the intake air temperature seems to have more effect on the DME and Methane emissions than a change in injection timing.

Figure 5.76: GC Data: BP15 in comparison to mixed mode combustion with 25% energy equivalent DME concentration and with 25% energy equivalent DME concentration at various injection timing and with increasing temperature.

Figure 5.77 shows Cylinder Pressure (bar) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As shown previously, with the addition of the 25% DME energy equivalent, the pressure trace shows a change from a distinct premixed and diffusion controlled phase of combustion to
a mostly premixed phase of combustion. With the addition of Methane to the DME, the pressure increases. A shift in the injection timing of the diesel fuel causes a shift in the combustion phasing of the peak pressure. Heating the intake air with this fuel scheme causes an increase in the peak pressure from the base condition by about 3 bar.

Figure 5.77: Cylinder Pressure (bar) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing
Figure 5.78 shows heat release rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. With the addition of Methane with DME into the intake air, the LTHR and the HTHR seem unaffected, but there is a decrease in the heat release from the diesel portion of the combustion. A shift in the injection timing of the diesel fuel causes an increase in the HTHR portion and the diesel fuel portion to be retarded. When using intake air heating, the LTHR and HTHR occur earlier in the combustion phasing while the combustion phasing and magnitude of the diesel combustion are the same in comparison for the cases of the three temperatures (25°C, 50°C, and 60°C). For the cases where no temperature is indicated, it should be assumed that this is the 25°C case. The LTHR is reduced, and the HTHR portion is increased as the intake air is heated.
Figure 5.78: Heat Release Rate (J/deg) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.

Figure 5.79 shows bulk cylinder temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing. As shown in
the figure, the Methane portion of the fumigated fuel increases the bulk temperature and advances the combustion phasing. With the retarding of the injection timing, the peak bulk temperature decreases, while the heat from the HTHR portion increases the bulk temperature. Increasing the intake air temperature serves to advance the LTHR peak and to increase both the HTHR peak and the main diesel fuel peak temperatures.
Figure 5.79: Bulk Temperature (K) for mixed mode combustion at 1800 rpm and 61 ft-lb torque with 25% DME energy equivalent with and without 5 SLPM (6.5% energy equivalent) Methane fumigated in the intake air at various intake air temperatures compared to BP15, at 7 and 1 ° BTDC fuel injection timing.
5.9 Discussion

The following sections discuss the data from the experiments described in this chapter. Each of the three sets of experiments were analyzed and results were separately shown. In this section, the key observations of these research studies will be discussed. These include:

- Reaction kinetics for DME that lead to the heat release
- Explanation for reduction in NO emissions and increase in NO$_2$ emissions
- Effect of injection timing and addition of heated intake air temperature
- Influence of HTHR on NO and main diesel combustion
- Observed hydrocarbons in the exhaust species
- Effect of Methane addition
- Effect of mixed mode combustion on particulate matter

5.9.1 DME Ignition and Reaction Kinetics

Pfahl and coworkers were able to measure the self-ignition behavior of diesel-relevant fuels as homogeneous mixtures using a high pressure shock tube [13]. Of the fuels they investigated, DME was also investigated in the temperature range of 650-1300K. They showed that DME exhibited a two step self ignition: a cool flame process at lower temperatures, followed by a negative temperature coefficient (NTC) region and a second detonation-like process [13].
Previously, many researchers have elucidated the reaction kinetics of dimethyl ether [23, 24, 26, 226, 227]. The oxidation chemistry is important in helping to understanding what is happening in this mixed mode combustion process, and in other diesel engine applications. Figure 5.80 shows the overall reaction scheme for dimethyl ether oxidation [24]. Curran and coworkers studied dimethyl ether oxidation in a variable pressure flow reactor over the temperature range of 550-850K, in the pressure range of 12-18 atm, and at equivalence ratios of $0.7 \leq \phi \leq 4.2$ [24]. Curran and coworkers also performed studies in a jet stirred reactor at 1 and 10 atm, $0.2 \leq \phi \leq 2.5$, and 800-1300K [23]. Dagaut and coworkers studies the oxidation and ignition of DME from 500-1100 K in a fused silica jet stirred reactor at 10 atm, and $0.2 \leq \phi \leq 1$ [228].
Both Curran and Dagaut’s research propose that the fuel initiation reactions occur by thermal decomposition of the fuel and reactions with $O_2$. Both researchers discuss the methoxymethyl radical ($CH_3OCH_2$) formed by H-atom abstraction on DME. From this reaction, the methoxymethyl radical further decomposes forming formaldehyde and $CH_3$, and reacts with $O_2$, $HO_2$, and $CH_3$. The formation of the methoxymethylperoxy radical
(CH$_3$OCH$_2$OO—simplified as RO$_2$) were included in Dagaut’s set of reactions, as well as a degradation reaction involving internal H-atom transfer yielding CH$_2$OCH$_2$OOH—simplified at QO$_2$H, self reactions and reactions with HO$_2$, DME and formaldehyde [228]. A kinetic analysis involving a sensitivity analysis and reaction paths analysis was used to interpret the results of Dagaut’s work. It was found that in the cool flame regions, the route R + O$_2$ $\rightarrow$ RO$_2$ $\rightarrow$QO$_2$H ( +O$_2$) $\rightarrow$ OQ’O +2OH dominates ( R here is CH$_3$OCH$_2$). The competition between the propagation and branching paths for QO$_2$H is responsible in his model for the observed NTC. Above a particular temperature that restarts the reactions in the second stage, the decomposition of R is favored and the formation of RO$_2$ becomes negligible [228].

While there has been much research into the reaction rates and pathways of DME ignition and oxidation, it is difficult to determine the appropriate reactions and radicals involved in this current research with DME and NOx mechanisms for an appropriate discussion. However, the work previously reported gives insight and an appropriate set of reactions for a model to be created.

### 5.9.2 Explanation for shift in NO to NO$_2$ emissions

According to work performed by Hori and coworkers, there is an effect of low concentrations of fuels on the conversion of NO to NO$_2$ [40, 229]. In their research, they show that the effectiveness of promoting the conversion depends on the type of fuel. They studied 7 different types of fuel, from H$_2$ and CH$_4$, to longer chain hydrocarbons like i-C$_4$H$_{10}$ and n- C$_4$H$_{10}$ [40]. Their work showed that the effectiveness increased with
increasing carbon chain length. Hori and coworkers went on to propose chemical kinetic reactions to explain the conversion of NO to NO₂ [40]. This conversion is indicated to proceed mainly through the NO + HO₂ → NO₂ + OH route. Therefore, if HO₂ is available in high quantities, the conversion is more effective [40]. In their conclusions, they also state that the temperature range of the conversion is important, but did not address which ranges. Also, they indicate that a C₃H₆ molecule would have a low conversion [40].

In Hori and coworkers later research, experiments and kinetic models were performed to further investigate the role of hydrocarbons in the NO to NO₂ conversion [229]. Five hydrocarbons were examined individually: methane, ethylene, ethane, propene, and propane. The results indicated that ethylene and propane are more effective than methane to oxidize the NO. Highest effectiveness comes as a result of hydrocarbons that produce reactive radicals like OH and O atoms, that promote oxidation and lead to the HO₂ production. If the hydrocarbon produces radicals, like methyl and allyl, which reduce the oxidation by O₂, this tends to reduce the NO₂ to NO through the reaction R + NO₂ → RO + NO ( R= CH₃ or aC₃H₅). Propane showed the greatest NO to NO₂ conversion at the lowest temperature and had the widest temperature range. Ethylene was also found to have similar effectiveness as propane. Methane and ethane were less effective.

Hori and coworkers research also showed that the effectiveness of the hydrocarbon is also dependent on the temperature range. While hydrocarbon consumption was accelerated when the reaction temperature increased, the reduction in NO₂ to NO was observed for longer residence times at the higher temperatures [229].
Hori and coworkers research helps to explain the shift in NO₂ to NO emissions seen in this research. In the decomposition of DME, HO₂ radicals are formed to propagate the reactions. In the series of DME reactions, methyl radicals are produced, which provide for the reaction route that shifts the NO₂ to NO. However, when the small quantity of Methane was introduced with the fumigated DME, this provided an additional pool of methyl radicals to the fumigated hot gases, which provided for some of the NO₂ to shift back to NO, and for the reaction route of CH₃ + HO₂ → CH₄ + O₂, as described by Curran and coworkers occurring at approximately 750K [24]. As shown in the mixed mode combustion results with DME and without Methane, there was a small amount of Methane being formed, indicating that this reaction route must have been occurring.

Dagaut and coworkers published some research about the low temperature oxidation of DME and its mutual sensitization with NO [26]. They showed that at temperatures below 600K, the oxidation of DME was inhibited by NO, but above 600K NO enhances the oxidation of DME in the cool flame regime and yields methylformate and an additional HO₂, which further provides the radicals to oxidize the NO to NO₂. The study showed that below 616K, the NO inhibits the oxidation of DME due to the removal of the methoxymethyl peroxy (CH₃OCH₂O₂) radical by reaction with NO, reducing the production of OH radicals and slowing the cool flame oxidation [26]. Above about 620K, the oxidation of DME and NO is due to the additional production of CH₃OCH₂O (also referred to as R) and OH which promote the oxidation in the following reactions: RO₂ + NO → RO + NO₂ and HO₂ + NO → OH + NO₂ [26].
5.9.3 Chemkin Modeling of DME HCCI

To determine if the HO$_2$ species was available in significant quantities, a model of a single cylinder from the DDC 2.5L engine was configured in Chemkin 4.1 to model the HCCI process of the DME combustion and ignition. Chemkin is a fortran library that was designed to aid in modeling the chemical kinetics of a reacting system [230]. As shown in the previous heat release plots for the mixed mode combustion, the DME combustion is occurring as a homogeneous charge prior to the diesel pilot fuel injection. Thus, an HCCI zero dimensional model will provide relevant kinetic information about the combustion. The high temperature and low temperature reaction mechanisms from Lawrence Livermore National Laboratory were used for the thermodynamic and reaction mechanism inputs [24, 25]. The system was assumed to be adiabatic with no heat loss and no wall heat transfer. The Chemkin model was programmed to start at the point that the intake valve closes, with an engine speed of 1800 rpm, and cycle through 1 crank revolution. The actual fuel and air for the testing was used to compute the mass fractions for the reaction species inputs, air and DME. Initial conditions were assumed to be 25 °C and 1 bar.

Figure 2.13 shows the fuel decomposition and select species pool of interest for the 25% energy equivalent DME HCCI. As shown, the HO$_2$ species is mode available from the DME decomposition and heat generated by the reaction and the compression. As the DME decomposition reaches completion, the amount of HO$_2$ production drops off, and the H$_2$O$_2$ species increases and plateaus. As shown in this model, not all of the DME is reacted through the compression of the fuel.
Figure 5.82 shows the Chemkin model of 25% energy equivalent DME HCCI with HO2 in comparison to other species of interest. In comparison, the production of HO2 far exceeds the production of the other species, thus making the NO to NO2 conversion possible. The Chemkin model confirms that HO2 is available at the time.
when NO would be produced from the diesel fuel portion of the combustion, as the injection of the diesel fuel occurs at -7° BTDC.

Figure 5.82: Chemkin model of 25% energy equivalent DME HCCI, A/F ratio of 138.1 and $\Phi = 0.065$, with HO$_2$ in comparison to other species (Initial Temperature 25 °C, Pressure 1 atm, Heat Loss 0.0 cal/sec)
Figure 5.83 shows that the HO$_2$ increases with increasing concentration of DME in the homogeneous charge. As shown, the increase is smaller between the 35% and 44% energy equivalent DME and than the 25% and 35% energy equivalent DME.

Figure 5.83: Chemkin model of 25% (A/F ratio of 138.1 and $\Phi = .065$), 35% (A/F ratio of 101.3 and $\Phi = .088$), and 44% (A/F ratio of 89.3 and $\Phi = .100$) energy equivalent DME HCCI showing increasing HO$_2$ species (Initial Temperature 25 °C, Pressure 1 atm, Heat Loss 0.0 cal/sec)
5.9.4 Injection Timing and Heated Intake Air Effect

In Figure 5.36, the injection timing of the diesel fuel is shown to only affect the ignition timing of the diesel fuel, with no apparent impact on the DME ignition. While it would be expected that the heat release from the diesel fuel portion would be lower when using the DME in a mixed mode combustion configuration because the amount of fuel being injected is less, it is unclear from the heat release and bulk temperature curves if the HTHR portion of the DME ignition contributes to a faster vaporization and additional heat release from the diesel fuel portion.

With retarded injection timing, the NOx emissions decrease with a decrease in the NO and NO\textsubscript{2} emissions. One could conclude that with the retarded timing, there is less time for thermal NO formation and also less time for the light hydrocarbon species to reach the NO and react to form NO\textsubscript{2}. With the retarded injection timing, the peak pressure finishes later, and the bulk temperature is lower for the diesel fuel portion of the heat release. As seen in Figure 5.35, the advanced injection timing pressure curve has a secondary peak, which merges into one peak as the injection timing is retarded. Also, the heat release is retarded in the same manner that the injection timing is retarded. The heat release rate is slightly higher with the retarded timing: 18\text{J/deg} for 7\textdegree\ BTDC versus 25 J/deg for 1\textdegree\ BTDC.

In the testing with the heated intake air system, an advance of the DME LTHR and HTHR was observed. With increasing intake air temperature, the LTHR portion decreases slightly, and the HTHR portion increases slightly. However, the temperature did not impact the timing of the diesel fuel ignition nor the magnitude. With increasing
intake air temperature, the bulk temperature increased. This resulted in an increase in the NOx emissions, with an increase in NO and a decrease in NO2. CO, Methane and total hydrocarbons were lower as the intake air was heated. Also, there was less DME present in the exhaust gas, so the heating allowed for greater combustion efficiency of the DME. The TEOM and SMPS data, Figures 5.63 and 5.64, showed that the intake air heating produced an increase in the total PM mass, and an increase in the number of particles observed in the accumulation mode.

5.9.5 Influence of High Temperature Heat Release from DME

As shown in Figures 5.13 and 5.24, with increasing DME concentration the NO emissions increase, with the high temperature heat release (HTHR) peak increasing and advancing towards the low temperature heat release (LTHR) peak. A similar trend is seen within the DME/Air HCCI work performed by Iida and Igarashi in a single cylinder Yanmar engine [231].

In Iida and coworkers’ research, they measured a reduction in NOx emissions in comparison to diesel fuel [231]. While NOx increased with equivalence ratio with diesel fuel, from 100 to almost 250 ppm from their single cylinder Yanmar engine running at 800rpm, for DME HCCI, the NOx were less than 50ppm [231]. However, the data does not reflect whether the NOx increase is due to NO or NO2. This research reflects a different trend with respect to NOx emissions, and further elucidates the data presented by Iida and coworkers. In this research, while the NOx emissions are still lower for the DME in a mixed mode combustion configuration, as the DME concentration is raised
beyond 25% energy equivalent, the amount of NO begins to increase and the NO₂ decreases. The magnitude of the HTHR peak at the 44% DME energy equivalent begins to approach the same magnitude of the diesel fuel heat release peak when running normal BP15 diesel, indicating that possibly the thermal NO mechanism is contributing more than the NO₂ pathways.

### 5.9.6 Hydrocarbons in Exhaust Species

As is seen with HCCI engines, hydrocarbon species in the exhaust system increase. In the case of this research, hydrocarbon species were seen to increase over normal diesel operation.

Total hydrocarbon species were collected with the AVL CEB II, and light hydrocarbon species were collected with a gas chromatograph. As shown in this research and expressed in the literature, light hydrocarbon species are present in exhaust when diesel fuel is used. In this mixed mode combustion configuration research with the DME and then with the DME/Methane blend, both species showed up in the GC results as unreacted species or species that were formed in the combustion process and frozen upon the exhaust stroke. However, other light hydrocarbons that would show up in the BP15 diesel fuel traces appeared but in much lower quantities in the mixed mode combustion configuration.

Based on the research by Hori and coworkers [40, 229], one could conclude that the light hydrocarbons that were present in the early part of the diesel spray vaporization and before its ignition, and in the gas phase oxidation around the diesel spray flame, were
able to participate in the low temperature combustion of the DME fuel and were involved in the NO to NO$_2$ conversion. It could be concluded that the light hydrocarbons from the diesel fuel spray were consumed in the reaction to produce the NO$_2$, and then the other hydrocarbons that were collected and show peaks in the GC must be from the DME fueling, which were mostly DME and Methane. The Methane contribution was higher when the mixed mode combustion configuration was fumigated with Methane. One could make this assertion because in all work with DME, very little if any of the light hydrocarbons show up in the GC traces, while with normal diesel operation they appear.

While most of the light hydrocarbon species from the combustion process for each test condition could be quantified, there were some species that appeared at various retention times that are unknowns. Figure 5.84 shows a GC trace for 25% DME energy equivalent mixed mode combustion at 7° BTDC. As is shown in this figure, there are two unidentified peaks. The first is located at 26.5 minutes and falling between dimethyl ether and the butane. The other peak is located at 29.5 minutes. It is unclear what either of these peaks may be. However, with this particular GC set up, the higher molecular weight molecules take a longer time to show up in the trace, so it would be possible to conclude that the first peak at 26.5 minutes has a molecular weight between 46 (DME) and 58 (Butane). It has been suggested that this peak may be butylene. The second peak is more difficult to determine, but it would have a molecular weight higher than 58.
Figure 5.84: GC Trace for 25% DME energy equivalent mixed mode combustion at 7° BTDC: FID trace in the later retention time (x-axis) region at 225°C
5.9.7 Effect of Methane Addition

Based on the data collected for the DME/Methane blends, it appears that the Methane served to increase the pressure and bulk temperature from the combustion process, and reduced the heat release from the diesel fuel portion. This led to lower NOx per power output, with higher NO and lower NO2 in comparison to the use of just DME as the fumigated fuel. While the Methane addition seemed to make a slight impact on the combustion of DME and resulted in 2-3ppm less in the exhaust, there were overall higher hydrocarbon emissions, mainly of unreacted Methane. The additional pressure and bulk temperature in the exhaust system provided more conversion of the CO to CO2, in comparison to a system with just DME.

According to research by Hori and coworkers, the Methane reactions in a low temperature environment would not support the reaction of NO to NO2 as effectively as some other hydrocarbons[229]. This is due to the slow oxidation of Methane that produces a limited amount of HO2, and the role of the methyl radicals in reducing NO2 via this reaction: CH3 + NO2 $\rightarrow$ CH3O +NO [229]. Thus, as seen in this research, the addition of a small amount of Methane to the fumigated fuel provided a larger pool of methyl radicals, as compared to the fumigation of DME alone, and resulted in an increase in the NO emissions in the exhaust gases as a result of the faster reaction of the NO2 reduction to NO [229]. This is also seen and supported in the work by Amano and Dryer, as the oxidation of Methane more readily occurs via the CH3 + NO2 $\rightarrow$ CH3O +NO reaction [232].
Combustion characteristics of a natural gas/DME mixture were studied numerically in a HCCI engine configuration [219]. This data was compared to experimental data collected by Chen and coworkers [214]. Kong confirmed that the low temperature heat release is more pronounced as the amount of DME increases within the natural gas/DME blend. His model also shows that as the natural gas and the DME concentration is increased, the amount of NOx emissions is decreased, confirming and comparing to the work by Chen and coworkers [219]. While it is important to note this work, and to note that Kong has provided temporal histories of combustion intermediate species, a direct comparison to the Methane and DME blend work cannot be made. Kong’s work does provide insight into the intermediate species from his model which would also be acting in this research [219]. Kong indicates that during the early chemical reactions, the concentrations of H$_2$O$_2$ and HO$_2$ increase rapidly before the first stage of ignition, with a small amount of OH forming. The species of H$_2$O$_2$ and HO$_2$ are associated with the low temperature heat release. As the compression continues and the intake air temperature rises, the temperature accelerates the decomposition of the H$_2$O$_2$ into OH radicals [219]. During the second stage of ignition, the concentration of H$_2$O$_2$ decreases as OH is formed. The decomposition of the H$_2$O$_2$ at about 1000K and the consumption of the remaining fuel results in ignition in Kong’s calculations [219].

5.9.8 Effect of Mixed Mode Combustion on particulate matter

Particulate Matter (PM) data from a TEOM and from an SMPS was collected in the experiments for this research. Total PM data was collected with the TEOM. With the
SMPS data, particles in the size range of approximately 6nm to 250nm were collected. Some BG-2 filters were collected to get an indication of the PM composition.

Total PM increased with increasing DME concentration, and was higher with DME in a mixed mode combustion configuration than with BP15 diesel fuel. Total PM also increased with retarded injection timing with the DME in a mixed mode combustion configuration. Also, Total PM increased with increasing intake air temperature with the DME in a mixed mode combustion configuration and was higher than with BP15 diesel fuel.

SMPS data showed that with the DME in a mixed mode combustion configuration the number of particles in the size range was reduced. Coupled with the TEOM data, this suggests that more large coarse particles were created with the DME in a mixed mode combustion configuration.

BG-2 filters were collected and digital pictures were presented. The BG-2 filters suggest that the PM with the DME in a mixed mode combustion configuration have more mass than with the conventional BP15 diesel fuel regardless of injection timing. Total hydrocarbon data shows that with the DME in a mixed mode combustion configuration, hydrocarbons are increased. Since the total amount of light hydrocarbons from the GC could not be completely quantified, it is unclear what the total is. However, from what was quantified, the GC showed approximately 30% of the hydrocarbons that were collected by the AVL CEB II in ppm. Therefore, there may have been some heavier hydrocarbons agglomerating on the PM.

The increase in PM with the DME in a mixed mode combustion configuration may be the result of the increased heating in the cylinder providing for a wider zone for
PM agglomeration and for a sustained time period. There were higher rates of PM formation. This was due to more soot precursors in and around the spray flame as a result of the shift in stoichiometry in the diesel spray flame due to DME competing for O₂ to oxidize. However, it is unclear whether all of the DME is being completely consumed, or if some of this is participating in the PM agglomeration. Further study of the PM through soxlet extraction of the BG-2 filters would provide an indication of the amount of hydrocarbons and other materials that have condensed on the PM in the combustion zone versus the purely soot portion.

5.10 Conclusions

For this research, a DDC 2.5L light duty turbocharged diesel was operated at 1800 rpm and 61 ft-lbs of torque, a BMEP of approximately 4.1. The engine was set to operate with a gaseous fuel fumigated in the intake air system, and with a single pulse injection of BP15 diesel fuel which was controlled for the entire set of research. All research data points were compared to the same fuel injection scheme with the normal BP15 diesel operation.

In the first set of experiments, DME concentration was spanned from 15% up to 44% on an energy equivalent basis. It was found that the lowest NOx emissions, and more specifically the lowest NO and highest NO₂ was at a 25% DME energy equivalent for a diesel pilot injection timing of 7° BTDC. For all DME concentrations, NOx was reduced by approximately 20% on a brake specific power basis. For the 25% concentration, NO was 50% lower, and NO₂ was over 140% higher in comparison to the
baseline diesel case. As the bulk cylinder temperature increased above about 1100K in
the second stage of the DME heat release, the NO to NO₂ conversion subsided, and
additional heating increased the thermal NO contribution. Chemkin modeling of a HCCI
system with DME showed an increase in the HO₂ concentration with increasing DME
concentration. As the HO₂ decreased, H₂O₂ increased, indicating temperature favoring
the production of hydrogen peroxide. Based on these results, the rest of the experiments
were performed at this 25% DME concentration test condition as the baseline mixed
mode combustion configuration.

The second set of experiments involved spanning the fuel injection timing of the
BP15 diesel fuel pilot. NOx emissions decreased with retarded injection timing, up to
40% in comparison to BP15 diesel emissions. Both NO and NO₂ emissions decreased.
While the bulk temperature was kept between 1000K and 1100K for a longer residence
time, the late injection timing of the diesel fuel relative to the 2ⁿᵈ stage heat release
(HTHR) of the DME did not provide additional conversion of NO to NO₂. It is unclear if
the temperature was too high for this conversion to occur, or if the availability of
hydrocarbon species to produce the HO₂ radicals and aid in the NO to NO₂ conversion
was lacking as a result of the late timing. However, the late timing resulted in lower
overall NOx emissions, and may be only the result of less time for thermal NO formation
from the diesel fuel spray heat release.

The third study utilized intake air heating to study its impact on the ignition and
combustion of DME, and on the NOx emissions. For all increases in the intake air
temperature, the NOx increased. The NO increased, but was still 50% less in comparison
to the BP15 baseline diesel fuel. NO₂ emissions were also decreasing with increasing
intake air temperature. With the increase in intake air temperature, the bulk temperature associated with the 2nd stage heat release (HTHR) was above 1200K. Therefore, the heating of the air may have been too high to effectively convert NO to NO₂, shortening this phase, and yet providing a longer time for thermal NO production. The GC data showed that with the increase in intake air heating, the small amount of DME that was present was decreasing and the amount of Methane that was being produced from the available methyl radicals was also decreasing. However, there was no significant increase in the NO₂ emissions. Again, this may indicate that a threshold temperature was reached where the NO to NO₂ conversion was not effective.

The final set of experiments involved fumigating the DME mixed mode combustion configuration with a small amount of Methane, 5 SLPM (6.5% energy equivalent), as well as taking an exploratory set of data on the effect of injection timing and intake air heating. With this small addition of Methane, a 5 % reduction in NOx emissions was observed over the DME mixed mode combustion configuration. NO emissions increased, while the NO₂ emissions decreased. As discussed previously, Methane is not considered as an effective hydrocarbon for the NO to NO₂ conversion, so the results of the NO and NO₂ seem reasonable in comparison to DME. The NOx reduction trend with injection timing of the diesel fuel pilot and the NOx increase with the intake air heating follow the same pattern as seen with the DME mixed mode combustion configuration presented before. It was clear from the pressure trace and heat release that the Methane was contributing to combustion process. While pressure was higher when using the Methane in comparison to the DME mixed mode combustion configuration, there was a suppression of the diesel fuel heat release.
While the results and discussion of this research provide some interesting insight into a DME mixed mode combustion configuration, there are many questions that arise from the research. Those will be presented and discussed in Chapter 6.
Chapter 6

Summary, Conclusions, and Suggestions for Future Work

6.1 Summary

Before stating conclusions deduced from the experimental data, the motivation and objectives of this research will be restated. The motivation for this research was to study strategies that could be used to reduce NOx emissions from compression ignition engines to meet current and future US EPA emissions regulations. There were two strategies that were studied:

1. Modifying the chemical structure of the fuel, specifically reducing the iodine value and thus saturation of methyl esters of biodiesel, to reduce the NOx emissions produced at the spray flame

2. Using a mixed mode combustion system to modify the combustion process

6.2 Observations and Conclusions

Based on the results presented in Chapters 4 and 5 for each of the NOx reduction strategies, the following observations and conclusions can be made.
6.2.1 NOx Reduction through fuel modification: Hydrogenated Biodiesel

Observations:

1. The 20% soy-based biodiesel blend showed increases in NOx emissions across the 4 engine modes.

2. The 40% soy-based biodiesel blend and both hydrogenated biodiesel blends showed NOx reductions for all 4 engine modes, and in all cases below the emissions levels for the conventional ULSD fuel.

3. The pressure, heat release rate, needle lift and bulk cylinder temperature figures are all very similar for each fuel tested. There was no correlation that could be made from minor changes in these figures to the amount of NOx emissions reduced.

4. If a higher adiabatic flame temperature indicates an increase in the NOx emissions as a result of the number of double bonds in the biodiesel fuel, then a decrease in those double bounds would lead to a decrease in the NOx emissions. This data and the adiabatic flame temperature calculation support this conclusion.

5. Fuel injection pressure increased as the needle lifted higher to deliver the required fuel in the same timing. This increase in fuel injection pressure and its affect on NOx emissions is unknown.

6. It may also be possible that the chemistry of the fuel affects the physical properties of the fuel as it is delivered into the cylinder. Specifically, that the higher density and lower volatility both produce a longer vaporization and a larger droplet spray field zone, thus causing higher NOx emissions. However, the
density of the B100 and H100 are similar, which does not explain the reduction in NOx result for the H20 and H40 fuel blends. The boiling range information for the neat fuels shows that the volatility of the biodiesel fuels are similar, and with higher volatility than the BP 15 diesel fuel. Thus, the higher volatility and shorter vaporization would lead to lower NOx emissions. Heat Release data showed similar vaporization, and yet lower NOx emissions with the H20 fuel.

7. Similar NOx results were shown with single vs. double injection of fuel.

Conclusions:

Based on the discussion regarding the theories for the biodiesel NOx effect, the results seen in the NOx emission data would have to be explained by the increase in adiabatic flame temperature for the soy-based biodiesel and the Prompt NOx effect as a result of the change in the biodiesel fuel properties between the soy-based biodiesel and the hydrogenated biodiesel. Also, the use of a neat fuel in the experiments would have provided for a greater difference in the NOx data, thus indicating the actual impact of the change in the chemistry of the hydrogenated biodiesel fuel.

6.2.2 NOx Reduction through Mixed Mode Combustion

First Set of Experiments: DME concentration spanned from 15% up to 44% on an energy equivalent basis

1. It was found that the lowest NOx emissions, and more specifically the lowest NO and highest NO₂ was at a 25% DME energy equivalent for a diesel pilot injection timing of 7° BTDC.
2. For all DME concentrations, NOx was reduced by approximately 20% on a power basis.

3. For the 25% DME energy equivalent concentration, NO was the 50% lower and NO₂ was over 140% higher in comparison to the baseline diesel case.

4. As was shown in the bulk temperature information, as the temperature increased above about 1100K in the HTHR of the DME heat release, the NO to NO₂ conversion subsided, and additional heating increased the thermal NO contribution.

5. Chemkin modeling of a HCCI system with DME showed an increase in the HO₂ concentration with increasing DME concentration. As the HO₂ decreased, H₂O₂ increased, indicating temperature favoring the production of hydrogen peroxide.

Conclusions:

In this system, greater utilization of DME did not produce a higher NOx reduction because of the increasing cylinder pressure driving up the adiabatic flame temperature of the fuels in the system and thus increasing the NO emissions. While the DME concentration in the intake increasing, the NOx were the same, but a greater amount of NO was converted to NO₂ because of the increasing HO2 concentration available.
Second Set of Experiments: Spanning the fuel injection timing of the BP15 diesel fuel pilot injection

1. NOx emissions decreased with retarded injection timing, up to 40% in comparison to BP15 diesel emissions. Both NO and NO₂ emissions decreased.

2. While the bulk temperature was kept between 1000K and 1100K for a longer residence time, the late injection timing of the diesel fuel injection and heat release did not provide additional conversion of NO to NO₂. It is unclear if the temperature was too high for this conversion to occur, or if the availability of hydrocarbon species to produce the HO₂ radicals and aid in the NO to NO₂ conversion was lacking as a result of the late timing.

3. The late timing resulted in lower overall NOx emissions, and may be only the result of less time for the thermal NO from the diesel fuel spray heat release.

Conclusions:

Earlier injection timing provides more time for NO to NO₂ conversion but with higher overall NOx emissions.

Third Set of Experiments: Utilized intake air heating to study the impact on the ignition and combustion of DME, and on the NOx emissions

1. For all increases in the intake air temperature, the NOx increased. The NO increased, but was still 50% less in comparison to the BP15 diesel fuel.

2. NO₂ emissions were also decreasing with increasing intake air temperature.
3. With the increase in intake air temperature, the bulk temperature associated with the DME HTHR was above 1200K. Therefore, the heating of the air may have been too high to effectively convert NO to NO₂, shortening this phase, and yet providing a longer time for thermal NO production.

4. The GC measurement of exhaust composition showed that with the increase in intake air heating, the small amount of DME that was present was decreasing and the amount of methane that was being produced from the available methyl radicals was also decreasing.

Conclusions:

Earlier retarded ignition of the DME would require cooling the intake air, thus providing more time for HO₂ production and NO to NO₂ conversion.

Fourth Set of Experiments: Fumigation of the DME Mixed Mode Combustion configuration with a small amount of methane, 5 SLPM (6.5% energy equivalent), as well as taking an exploratory set of data on the effect of injection timing and intake air heating

1. With this small addition of methane, a 5 % reduction in NOx emissions was observed over the DME Mixed Mode Combustion configuration.

2. NO emissions increased, while the NO₂ emissions decreased.

3. The NOx reduction trend with injection timing of the diesel fuel pilot and the NOx increase with the intake air heating follow the same pattern as seen with
the DME Mixed Mode Combustion configuration: as timing is retarded, NOx decreases and as intake air is heated, NOx increases.

4. It was clear from the pressure and heat release rate figures that the methane was contributing to combustion process. While pressure was higher when using the methane in comparison to the DME Mixed Mode Combustion configuration, there was a suppression of the diesel fuel heat release.

Conclusions:
The presence of the methane, and therefore the methyl radical in the presence of NO₂ provided for the reaction \( CH₃ + NO₂ \rightarrow CH₃O + NO \), and thus the oxidation and utilization of methane to occur in the system.

6.3 Suggestions for Future Work

Upon examination of the results and conclusions, it is apparent that this research could be extended to gain further insight. The suggestions for further work will be discussed by the strategy that was researched.

6.3.1 NOx Reduction through fuel modification: Hydrogenated Biodiesel

While the research aimed to demonstrate that the hydrogenated biodiesel fuel could reduce NOx emissions, there were some theories that were not addressed and some questions that deserve further research.
1. Comparison of the hydrogenated biodiesel fuel to other researchers’ data should be pursued if possible. However, performing further experiments with the hydrogenated biodiesel fuel with modifications of fuel injection parameters, engine turbocharger and EGR parameters may yield more explanation of why this particular engine is yielding lower NOx emissions while other researchers are showing neutral or increase NOx emissions with methyl oleate.

2. A study of the effect of fuel injection pressure could be completed, with holding the injection timing constant and observing the change in exhaust emissions based on changes in injection pressure of the fuel spray.

3. The work by Boulanger and coworkers suggests that isolating the physical properties of the methyl esters can provide insight through experimentation and modeling of the physics of the process [204]. Specifically, comparing methyl oleate and methyl linoleate would explain what is found with changes in biodiesel chemical composition.

4. Experimental work in spray break up and droplet vaporization time scales would be useful to explain the onset of ignition for different methyl esters.

5. Imaging of biodiesel fuel spray, plume size and thermal mapping similar to the work by Dec [15, 29, 233] would be useful to determine if the burning of the biodiesel is creating a reduced area for NOx production in relation to the temperature of the flame zone.
6.3.2 NOx Reduction through Mixed Mode Combustion

While the research aimed to demonstrate a mixed mode combustion system with as much NOx reduction as possible, there are observations that suggest further research.

1. After reviewing the diesel pilot injection data, it appears that advancing the pilot diesel to 9 ° BTDC or earlier may have allowed for a higher DME content to be used, and thus reduced the heat release from the HTHR DME as a result of the diesel fuel pilot vaporization. This may delay the onset of H₂O₂ production, and increase the HO₂ radical for greater NO to NO₂ conversion.

2. There are other methods that would essentially reduce the fast heat release of HTHR DME ignition, prolonging the low temperature combustion and conversion of the NO to NO₂. This might include the use of EGR or some gaseous fuel that slows the kinetics of the second stage heat release. Also, liquid fuels that would form light hydrocarbons through pyrolysis would be of interest since those components would potentially be involved in the low temperature combustion in the reactions outside of the fuel spray.

3. Based on the work by Hori [40, 229], the suggestion that propane and ethane would produce more conversion of NO to NO₂ in the low temperature combustion would be of interest to study in combination with DME. The radical contribution of the propane may increase the temperature range for the conversion, and produce a greater result.
4. Use of a motored engine would provide a means to study the partial oxidation products in the exhaust through adjustment of the compression ratio and quenching of the exhaust after partial combustion [234]. This would help explain the types of gaseous hydrocarbons in the exhaust in this mixed mode combustion process.

5. Some further work into understanding the increase in particulate matter mass is suggested by this data. While much research into DME shows that this and many other oxygenates reduce particulate matter emissions, it is unclear why this mixed mode combustion process would be producing more particulate matter.

6. To assist in elucidating what occurs in the HCCI combustion process of DME and DME /methane blend, a series of models could be developed with Chemkin. The chemical mechanisms for methane combustion have been available for some time, and the mechanisms for DME combustion have been developed by several groups [23, 235]. It seems that the mechanisms developed by Lawrence Livermore National Laboratory are the most common set in use [23, 142]. These could be incorporated with NOx mechanisms (if not already available in the DME and methane mechanisms) so that the model can yield NO and NO$_2$ predictions. It would be important to consider the work by Hori and Dagaut in the NOx modeling mechanisms selection[26, 229]. Researchers have shown that simple zero dimensional kinetic models are sufficient to predict the combustion process in an HCCI engine, since the heat release is a global non-propagating autoignition process [142]. In the case of a pilot injection of fuel, the modeling becomes more difficult as CFD code would be required to completely model the system.
7. Using combustion video of the engine combustion process may provide more significant indication of what is occurring during the process. While flame luminosity in the infrared and normal light would show the diesel flame ignition, the DME cool flame would be best observed by ultraviolet light. Thus, a camera and filters capable of both would provide the best inspection and evidence of continued experimentation with DME in a mixed mode combustion process.
Bibliography


## Appendix A

### TEOM Instrument File Configuration and User Configuration

#### A.1 Instrument File Configuration

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- **Channel 2**: Contents 84, Minimum Point -2.50E+00, Maximum Point 22.5
- **Channel 3**: Contents 85, Minimum Point 0.00E+00, Maximum Point 1.00E-04
- **Serial Output**: Contents 83, Minimum Point -116 | C, Step 0.1
- **Key Assign F1**: Contents | Units -116 | C, Minimum Point 49.8, Step 0.1
- **Key Assign F2**: Contents | Units -117 | C, Minimum Point 49.8, Step 0.1
- **Key Assign F3**: Contents | Units -118 | C, Minimum Point 49.8, Step 0.1
- **Key Assign F4**: Contents | Units -119 | C, Minimum Point 44.8, Step 0.1
- **Key Assign F5**: Contents | Units 83 | g/s, Minimum Point -2.50E-07, Step 2.50E+00
- **Key Assign F6**: Contents | Units 84 | mg/m^3, Minimum Point -2.50E-07, Step 2.50E+00
- **Key Assign F7**: Contents | Units 88 | Hz, Minimum Point 200, Step 2.00E-05
- **Key Assign F8**: Contents | Units 89 | SD, Minimum Point 0.00E+00, Step 1.00E+06
- **Key Assign F9**: Contents | Units 90 | in. HG, Minimum Point -122, Step 0
- **Key Assign F10**: Contents | Units -122 | in. HG, Minimum Point 0, Step 5
Appendix B

Biodiesel and Ultra Low Sulfur Diesel Fuel Specification Reports

B.1 Biodiesel Fuel Specification

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Data provided on normal biodiesel samples from Mike Haas at the USDA.

Sample 1 is from the barrel of fuel used in testing. Sample 2 is from a barrel from the sample batch for comparison.
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<td>Total Glycerine</td>
<td>D6584</td>
<td>% mass</td>
<td>0.240 max.</td>
<td>0.050-0.15</td>
</tr>
<tr>
<td>Phosphorus Content</td>
<td>D4951</td>
<td>% mass</td>
<td>0.001 max.</td>
<td>0.0002-0.0005</td>
</tr>
<tr>
<td>Distillation Temperature</td>
<td>D1160</td>
<td>Degrees ºC</td>
<td>360 max.</td>
<td>350</td>
</tr>
<tr>
<td>Temperature, Atmospheric</td>
<td></td>
<td>Degrees ºF</td>
<td>680 max.</td>
<td>662</td>
</tr>
<tr>
<td>Equivalent Temperature, 90%</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Recovered</td>
<td>UOP391</td>
<td>ppm</td>
<td>5ppm max.</td>
<td>&lt;2</td>
</tr>
</tbody>
</table>
### The "Gold Standard" of Biodiesel

**SOYGOLD**

A BQ-9000 Accredited Producer

June 21, 2006

<table>
<thead>
<tr>
<th>Property</th>
<th>ASTM Method</th>
<th>Units</th>
<th>Non-ASTM Standards</th>
<th>SoyGold Standard Ranges</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Gravity Density@60°F</td>
<td>D4052</td>
<td>Sp. Gr. Pounds/Gallon API° Lbs/ Cu. Ft</td>
<td>Report</td>
<td>0.8843 7.5695 28.56 55.1578</td>
</tr>
<tr>
<td>Soap</td>
<td></td>
<td>PPM</td>
<td>Report</td>
<td>ND</td>
</tr>
<tr>
<td>Rancimat@110 °C</td>
<td>EN14112</td>
<td>Hours</td>
<td>3.0</td>
<td>3.0-6.0</td>
</tr>
<tr>
<td>NACE Corrosion@72°F</td>
<td>TM0172-2001</td>
<td>B+ min.</td>
<td></td>
<td>A-B++</td>
</tr>
<tr>
<td>HAZE RATING @60°F</td>
<td>D4176</td>
<td></td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Voluntary Filtration Method</td>
<td>D6217 Modified (B)</td>
<td>Seconds</td>
<td>360 max.</td>
<td>20-200</td>
</tr>
</tbody>
</table>

| METALS/OTHER*                     | ICP         | PPM | Report | < 0.50 |
| Ca + Mg                           |             |     |        | < 0.10 |
| Cu-Copper                         |             |     |        | < 0.15 |
| Na-Sodium                         |             |     |        | < 1.00 |
| Ca-Calcium                        |             |     |        | < 1.00 |
| Mg Magnesium                      |             |     |        | < 0.15 |
| P-Phosphorous                     |             |     |        | < 1.60 |
| Fe-Iron                           |             |     |        | < 0.20 |
| Ni-Nickel                         |             |     |        | < 0.20 |
| K-Potassium                       |             |     |        | < 1.00 |

* Metal-Less than 0.05 PPM reported as "ND" (Non-Detect)
Certificate of Analysis

Load Order: 890-7584
Shipping date: 5/8/2006
Rail/Truck #: CPT 137 T 388

Customer: AG Environmental Products
Attn: 
Street: 12700 West Dodge Road
P.O. Box: 2047
City: Omaha
State: NE
Zip code: 68103-2047

Customer PO: 
Schedule PO: 

Product ID: 99600
Product name: SOYGOLD Soy Diesel

Lot number: B605-08b (CB050806)

Total glycerin: 0.096%
Free glycerin: 0.011%
Acid Number: 0.15 mg KOH/gram
Moisture: 0.0287%
Methanol: 0.058%
Soap: 0 ppm
Additive: None

Prepared by: Becky Still
AG Processing Inc. Methyl Ester Plant

Monday, May 08, 2006
### B.2 Hydrogenated Biodiesel Fuel Specification

**RBHD Soybean Ester Release**

**Lot Number**  ED60466-2

<table>
<thead>
<tr>
<th>Analysis</th>
<th>Specification</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>% FFA</td>
<td>0.10% max</td>
<td>0.05</td>
</tr>
<tr>
<td>440nm Transmittance</td>
<td>90 % min</td>
<td>97.93%</td>
</tr>
<tr>
<td>550nm Transmittance</td>
<td>95 % min</td>
<td>99.77%</td>
</tr>
<tr>
<td>% C 12</td>
<td>1.0 % max</td>
<td>0</td>
</tr>
<tr>
<td>% C 14</td>
<td>1.0 % max</td>
<td>0.07</td>
</tr>
<tr>
<td>% C 16</td>
<td>8.5 - 13.5%</td>
<td>11.0</td>
</tr>
<tr>
<td>% C 18</td>
<td>80 - 92%</td>
<td>85.07</td>
</tr>
<tr>
<td>PV</td>
<td>85 ppm max</td>
<td>NF</td>
</tr>
<tr>
<td>CV</td>
<td>200 ppm max</td>
<td>74</td>
</tr>
<tr>
<td>% Glycerine</td>
<td>150 ppm max</td>
<td>121</td>
</tr>
<tr>
<td>% Glycerides</td>
<td>500 ppm max</td>
<td>0</td>
</tr>
<tr>
<td>% Moisture</td>
<td>0.1 % max</td>
<td>NF</td>
</tr>
</tbody>
</table>

**Approval Status**

This Batch is: **accepted / redistilled / blended**

Approved by: [Signature]

(Trillant Technician)

1/27/2004

RBHD Soybean Ester Release Rev. 1
Acid Summary Report
4/6/08 00:55 PM

Sample Code: ED60406-2
Analyzer: WB
Data File: C:\HPCHEM2\DATA\04042006\APR6F001.D

Instrument: US00009973
Acquisition Method: FACb.M
Acquisition Date: 4/6/06 20:40

Fatty Acid Chainlength Distribution

<table>
<thead>
<tr>
<th>Chain Length</th>
<th>ME</th>
</tr>
</thead>
<tbody>
<tr>
<td>C12 ME</td>
<td>0.00</td>
</tr>
<tr>
<td>C14 ME</td>
<td>0.07</td>
</tr>
<tr>
<td>C16 ME</td>
<td>10.86</td>
</tr>
<tr>
<td>C17 ME</td>
<td>0.09</td>
</tr>
<tr>
<td>C18 ME</td>
<td>0.00</td>
</tr>
<tr>
<td>C20 ME</td>
<td>0.30</td>
</tr>
<tr>
<td>C21 ME</td>
<td>0.00</td>
</tr>
<tr>
<td>C22 ME</td>
<td>0.67</td>
</tr>
<tr>
<td>C23 ME</td>
<td>0.00</td>
</tr>
<tr>
<td>C24 ME</td>
<td>0.00</td>
</tr>
<tr>
<td>C16=1 ME</td>
<td>0.14</td>
</tr>
<tr>
<td>C17=1 ME</td>
<td>0.07</td>
</tr>
<tr>
<td>Total C16=1 ME</td>
<td>11.00</td>
</tr>
<tr>
<td>Total C18=2 ME</td>
<td>18.44</td>
</tr>
<tr>
<td>Total C18=3 ME</td>
<td>0.07</td>
</tr>
<tr>
<td>Total C20=1 ME</td>
<td>0.32</td>
</tr>
<tr>
<td>Total C22=1 ME</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Summary Report

<table>
<thead>
<tr>
<th>Total</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total C16</td>
<td>11.00</td>
</tr>
<tr>
<td>Total C18</td>
<td>85.57</td>
</tr>
<tr>
<td>Total C22</td>
<td>0.07</td>
</tr>
</tbody>
</table>

% Total Saturated Fatty Acid: 11.40

% Total Acid: 100.00
% Total Unknown: 0.00

Iodine value: 93.3
Total Area: 20436
Sample: ED60406-2

Method: Fatty Acid Composition
Method #: OMGC-03-0197
Analyst: WB

Injected On: 4/6/06 8:42 - 4/6/06 8:40:5 - Acquisition Method: FACB.M

Raw Data File: C:\HPCHEM\2\DATA\04042006\APR6F001.D
Sequence: C:\HPCHEM\2\SEQUENCE\OMEGA3B.S

Method Last Modified: 4/6/06 5:03:19 AM
Vial #: 1.000

#  Meas. Ret.  Exp. Ret.  Area  Compound Name  Area %
1    0.000    1.566    0.0   C12 ME   0.000
2    2.374    2.376    15.3  C14 ME   0.075
3    3.408    3.400    2219.9  C16 ME  10.863
4    3.538    3.542    28.0  C16=1 ME  0.137
5    4.035    4.012    19.3  C17 ME   0.095
6    4.190    4.150    14.7  C17=1 ME  0.072
7    0.000    4.800    0.0   C18 ME   0.000
8    0.000    4.980    0.0   C18=1 ME  0.000
9    5.066    5.102    11812.1  C18=1 ME 57.801
10   5.153    5.135    2240.1  C18=1 ME 10.962
11   0.000    5.175    0.0   C18=1 ME  4  0.000
12   0.000    5.235    0.0   C18=1 ME  5  0.000
13   0.000    5.300    0.0   C18=2 ME  1  0.000
14   5.388    5.350    3213.8  C18=2 ME  2 15.726
15   5.467    5.470    463.4  C18=2 ME  3  2.267
16   5.614    5.640    26.7  C18=2 ME  4  0.131
17   0.000    5.760    0.0   C18=3 ME  1  0.000
18   5.870    5.874    157.2  C18=3 ME  2  0.769
19   5.986    5.988    20.5  C18=3 ME  3  0.100
20   6.195    6.090    29.3  C18=2 ME  5  0.144

C:\HPCHEM\2\DATA\04042006\
## Analytical Report

<table>
<thead>
<tr>
<th>#</th>
<th>Meas. Ret.</th>
<th>Exp. Ret.</th>
<th>Area</th>
<th>Compound Name</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>6.182</td>
<td>6.180</td>
<td>34.4</td>
<td>C18=2 ME 6</td>
<td>0.168</td>
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<tr>
<td>22</td>
<td>0.000</td>
<td>6.189</td>
<td>0.0</td>
<td>C18=2 ME 7</td>
<td>0.000</td>
</tr>
<tr>
<td>23</td>
<td>6.509</td>
<td>6.507</td>
<td>61.8</td>
<td>C20 ME</td>
<td>0.302</td>
</tr>
<tr>
<td>24</td>
<td>0.000</td>
<td>6.620</td>
<td>0.0</td>
<td>C18=2 ME 8</td>
<td>0.000</td>
</tr>
<tr>
<td>25</td>
<td>6.664</td>
<td>6.670</td>
<td>65.3</td>
<td>C20=1 ME</td>
<td>0.320</td>
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<tr>
<td>26</td>
<td>0.000</td>
<td>7.342</td>
<td>0.0</td>
<td>C21 ME</td>
<td>0.000</td>
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<tr>
<td>27</td>
<td>8.152</td>
<td>8.200</td>
<td>14.0</td>
<td>C22 ME</td>
<td>0.068</td>
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<tr>
<td>28</td>
<td>0.000</td>
<td>8.940</td>
<td>0.0</td>
<td>C22=1 ME</td>
<td>0.000</td>
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<tr>
<td>29</td>
<td>0.000</td>
<td>9.150</td>
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<td>30</td>
<td>0.000</td>
<td>9.814</td>
<td>0.0</td>
<td>C24 ME</td>
<td>0.000</td>
</tr>
</tbody>
</table>

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**Total Area:** 20436
### Certificate of Analysis

**Conoco BP-15 Diesel Fuel**  
**Issue date:** July 18, 2002  
**RE:** Conoco BP-15 Diesel Fuel 21071-70

<table>
<thead>
<tr>
<th>TEST</th>
<th>TEST METHOD</th>
<th>SPECIFICATION</th>
<th>RESULT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cetane Index (calculated)</td>
<td>ASTM D-976</td>
<td>report</td>
<td>48.8</td>
</tr>
<tr>
<td>Cetane Number (engine rating)</td>
<td>ASTM D-613</td>
<td>report</td>
<td>49.7</td>
</tr>
<tr>
<td>Corrosion, Cu Strip, 3hr. @ 122°F</td>
<td>ASTM D-130</td>
<td>report</td>
<td>1a</td>
</tr>
<tr>
<td>Distillation, degrees F</td>
<td>ASTM D-86</td>
<td>report</td>
<td></td>
</tr>
<tr>
<td>IBP</td>
<td></td>
<td></td>
<td>330.3</td>
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<tr>
<td>T50</td>
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<td>500.7</td>
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<tr>
<td>FBP</td>
<td></td>
<td></td>
<td>653.9</td>
</tr>
<tr>
<td>Specific Gravity @60°F</td>
<td>ASTM D-4052</td>
<td>report</td>
<td>.8374</td>
</tr>
<tr>
<td>Polycyclic aromatic hydrocarbon</td>
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<td>report</td>
<td>6.9</td>
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<tr>
<td>Content, GC-SFC, wt%</td>
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<td></td>
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<tr>
<td>Carbon residue</td>
<td>ASTM D-524</td>
<td>report %</td>
<td>0.04</td>
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<tr>
<td>Flash point Pensky Martin °F</td>
<td>ASTM D-93</td>
<td>report</td>
<td>147</td>
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<tr>
<td>Viscosity at 40°C cSt</td>
<td>ASTM D-445</td>
<td>report</td>
<td>2.5</td>
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<tr>
<td>Pour point °F</td>
<td>ASTM D-97</td>
<td>report</td>
<td>-0.4</td>
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<tr>
<td>Cloud point °F</td>
<td>ASTM D-5773</td>
<td>report</td>
<td>10.4</td>
</tr>
<tr>
<td>Sulfur, Total</td>
<td>ASTM D-2622</td>
<td>&lt;15 ppm W</td>
<td>13 ppm W</td>
</tr>
<tr>
<td>Lubricity, Boccle Pass</td>
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<tr>
<td>Lubricity, Boccle Fail</td>
<td>Report</td>
<td></td>
<td>4500</td>
</tr>
</tbody>
</table>
VITA

Elana M. Chapman

EDUCATION
M.S. in Mechanical Engineering, Spring 2008.
M.S. in Fuel Science, August 2002.
Pennsylvania State University, University Park, PA.
Bachelor of Science in Mechanical Engineering, University of Dayton, Dayton, OH, May 1992.

RESEARCH PUBLICATIONS


